P. 480

Adv. 9.17. (Bathe)

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Physics 481 – Advanced Quantum Mechanics.

Prof. Bethe – Rockefeller Hall – Room 104

Topics to be covered:

Matrix Mechanics
Oscillators
Angular Momentum.
Transition Probabilities (all in Condon + Shortley)

Transformation Theory.

Group Theory [Complex Spectra: Wigner, von Neumann 1927-29
Slater, Hund, Pauli, no group theory 1930-32

Then appl. to crystals
also to nuclear physics, Wigner

Relativistic Wave Eqn of Dirac.

Radiation theory, + Quantum Electrodynamics.

Books recommended:

Rojansky – esp. on Matrix Mech.

Kramers (Hand- + Jahrbuch d. chemischen Physik 1)
esp. on Transformation theory.
and on adiabatic perturbations.

Wigner – on groups theory

Dirac – esp. on Relat. Wave Eqn.

Pauli - Handbuch XXIV - 1 - esp. on Dirac eqn, and on radiation & quantum electrodynamics

Fermi. - R.M.P. on radiation -

I Matrix Mechanics.

Consider a transformation changing a point x to a point y.

then the coordinates y_i are functions of the x_i;

$$\left.\begin{aligned} y_1 &= \sum^{3} a_{1i} x_i \\ y_2 &= \cdots \\ y_3 &= \cdots \end{aligned}\right\} \text{ or } y = Ax$$

matrix of transformation : $\begin{pmatrix} a_{11} & a_{12} & \cdots \\ - & a_{22} & \cdots \\ - & - & a_{33} \end{pmatrix} \equiv A$.

suppose also $z = By$;

then $z = BAx$

$$z_i = \sum b_{ij} y_j = \sum b_{ij} \sum a_{jk} x_k$$
$$= \sum c_{ik} x_k$$

matrix multiplication $\longrightarrow$ where $c_{ik} = \sum_j b_{ij} a_{jk}$

$$z = Cx, \quad C = BA.$$

in general $AB \neq BA$. non-commutative -

but distributive law holds: $A(BC) = (AB)C$.

and $A(B+C) = AB + AC$.

Rotation of space : vectors y & x have same length:

$$|y| = |x| -$$

or $\sum y_i^2 = \sum x_i^2$

Therefore must have:

$$\sum y_i^2 = \sum x_i^2$$

$$\sum_i \left(\sum_j a_{ij} x_j\right)^2 = \sum x_i^2$$

$$\sum_{ikl} a_{ik} a_{il} x_k x_l = \sum x_i^2$$

$$\therefore \quad \sum a_{ik} a_{il} = \delta_{kl}$$ orthogonality normality

Define $\tilde{A}$, transpose matrix

$$\tilde{A}_{ij} = A_{ji}$$

$$\therefore \quad \sum a_{ik} \tilde{a}_{li} = \delta_{kl}$$

$$\text{or } (\tilde{A} A)_{kl} = \delta_{kl} = 1$$

$$\therefore \tilde{A} A = 1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Unitary ~~transformation~~

If $x_1\ x_2\ x_3$ are complex:

$$|x|^2 = \sum x_i x_i^*$$

a's are complex;

rotation: $\sum |y_i|^2 = \sum_i \left(\sum_k a_{ik} x_k\right)\left(\sum_l a_{il}^* x_l^*\right) = \sum (x$

$$\therefore \sum a_{ik} a_{il}^* = \delta_{kl}$$

Define $\tilde{A}^*$: $(\tilde{A}^*_{li}) = (a_{il})^*$

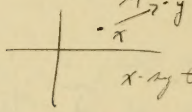
$\tilde{A}^*$: ~~conjugate transpose~~ $\quad \therefore \tilde{A}^* A = 1$

Unitary Matrix ≡ rotation of space

$$\tilde{A}^* A = 1$$

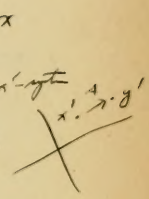
can also rotate coordinate instead of rotating space : also represented by unitary matrix

Consider a mapping A :



$$y = Ax$$

" same mapping in a different coord. system :



$$x' = Sx$$
$$y' = Sy$$
$$\therefore y' = SAx$$

Now introduce inverse matrix S^{-1} : $SS^{-1} = 1$
$S^{-1}S = 1$

For a unitary matrix : $S^{-1} = \tilde{S}^*$

$$\therefore \quad S^{-1}x' = S^{-1}Sx = x$$

$$\therefore y' = SAx = SAS^{-1}x'$$

$$\therefore y' = A'x', \quad A' = SAS^{-1}$$

also $S^{-1}A'S = S^{-1}SAS^{-1}S = A$

$$\therefore A = S^{-1}A'S$$

Can we diagonalize A?

$\cancel{A = \varepsilon 1}$

$\cancel{A - \varepsilon 1 = 0}$

? : $y = Ax = \varepsilon x$

$(A - \varepsilon 1)x = 0$

only soluble if $|A - \varepsilon 1| = 0$

or $\begin{vmatrix} a_{11}-\varepsilon & a_{12} & a_{13} \\ a_{21} & a_{22}-\varepsilon & a_{23} \\ a_{31} & a_{32} & a_{33}-\varepsilon \end{vmatrix} = 0$ can find 3 ε's

which will transform A to principal axes - three

direction along which there is only compression or expansion.

Ratio $x_1 : x_2 : x_3$ given

If $x_1 : x_2 : x_3 = \alpha : \beta : \gamma$, then $y_1 : y_2 : y_3 = \alpha : \beta : \gamma$

$$y = \varepsilon x$$

Then transform to principal system: $A' = \begin{pmatrix} \varepsilon^{(1)} & 0 & 0 \\ 0 & \varepsilon^{(2)} & 0 \\ 0 & 0 & \varepsilon^{(3)} \end{pmatrix}$

where $\varepsilon^{(1)(2)(3)}$ are roots of $|A - \varepsilon I| = 0$

Now to Quantum Mech.

Operate on a $\psi(x, t)$ with A: $A\psi$

A ~~contains~~ $A = A(x, \frac{\partial}{\partial x} \cdots)$ (not time)

Suppose ψ is n^{th} eigenf'n of some dynamical problem $\psi_n = u_n(x) e^{-\frac{i}{\hbar} E_n t}$

then $A\psi_n$ is not in general an eigenf'n.

But if we know all the eigenf'ns, we can expand in terms of them:

$$A u_n = \sum_m a_{nm} u_m \quad \left(+ \int a_n(m) u(m) dm \right) \text{ if cont. spectrum}$$

$$a_{nm} = \int u_m^* A u_n \, dx \quad , \text{ since } u_n \text{ are orthonormal}$$

Suppose $\psi = \sum_n c_n \psi_n = \sum b_n u_n e^{-}$

$$A\psi = \sum_n b_n \sum_m a_{nm} u_m = \sum \bar{b}_m u_m$$

then $\bar{b}_m = \sum_n a_{nm} b_n$

just like $y_i = \sum a_{ij} x_j$

$\therefore$ b's are analogous to coordinates in ordinary space;

a f'n ψ can be represented by its "coordinates" b_n

"Hilbert space" – infinite no. of dimensions; each axis corresp. to a quantum state (mathematically, to one of the characteristic f'ns of an orthonormal set)

Any wave f'n ψ is represented by a pt. in Hilbert space.

Any operation A corresponds to a mapping in Hilbert space.

$$b_n = c_n e^{-\frac{i}{\hbar} E_n t} \qquad A\psi = \sum \bar{c}_m \psi_m$$

introduce $\bar{c}_m = \bar{b}_m e^{\frac{i}{\hbar} E_m t}$

$$\bar{c}_m = \sum_n a_{nm} e^{\frac{i}{\hbar}(E_n - E_m)t} c_n$$

$$= \sum_n A_{nm} c_n \qquad A_{nm} = a_{nm} e^{\frac{i}{\hbar}(E_n - E_m)}$$

(sometimes use time-dependent, sometimes time-independent coeff's)

10/1/40 operator A : wave f'n ψ :

can expand ψ and $A\psi$ in terms of eigen f'n's.

$$A\psi = \sum_n b_n \psi_n \qquad \psi = \sum_n c_n \psi_n$$

$$b_n = \sum_m a_{nm} c_m \qquad a_{nm} = \int \psi_n^* A \psi_m$$

if $A = A(x)$ and real, $a_{nm} = a_{mn}^*$: Hermitean matrix

$$\tilde{A}^* = A. \qquad (\text{Unitary} : \tilde{A}^* = A^{-1})$$

if $A = A(p)$ and real

(1) $A = p = -i\hbar \frac{\partial}{\partial x}$; $p_{mn} = -i\hbar \int \psi_n^* \frac{\partial \psi_m}{\partial x} = +i\hbar \int \frac{\partial \psi_n^*}{\partial x} \psi_m$

$$p_{nm} = -i\hbar \int \psi_m^* \frac{\partial \psi_n}{\partial x} = p_{mn}^* \quad \therefore p \text{ is Hermit}$$

consider two operators A & B:

$$AB\psi = \sum_n d_n \psi_n$$

$$\cancel{d_n = \sum_m (AB)_{nm} c_m}$$

$$\cancel{= \sum_m \sum_j a_{mj} b_{jn} c_m}$$

Hereafter $A_{mn} = \int \psi_m^* A \psi_n$

etc.

$$AB\psi = \sum d_n \psi_n \; ; \quad (AB)_{mn} = \int \psi_m^* AB \psi_n$$

$$B\psi_m = \sum_l b_{ml} \psi_l \qquad = \int \psi_m^* A \sum_l b_{ln} \psi_l$$

$$= \sum_l \int \psi_m^* A \psi_l = \sum b_{ln} a_{ml}$$

$$= \sum_l b_{ml} \int \psi_n^* \sum = \sum_l a_{ml} b_{ln}$$

$\therefore$ Matrices representing waves; mult.

Operators follow laws of matrix algebra.

Matrix of p is Hermitean; hence also p^2;

for $p^2_{mn} = \sum_l p_{ml} p_{ln} = \sum_l p_{lm}^* p_{nl}^* =$

$p^2_{nm} = \sum_l p_{nl} p_{lm} = (p^2_{mn})^*$

likewise p^n is Hermitean;

Hence any power-series-representable function is Hermitean

Hence all ordinary f^ns of x & p are Hermitean

~~also $f(x)g(p)$ is Hermitean~~;

$\therefore$ any real function of x's & p's is represented by a Hermitean Matrix.

Commutation

in general $AB \neq BA$.

e.g. $[px - xp] = -i\hbar\left[\frac{\partial}{\partial x}x - x\frac{\partial}{\partial x}\right] = -i\hbar\left[x\frac{\partial}{\partial x} + 1 - x\frac{\partial}{\partial x}\right]$

$= -i\hbar$.

commutator is diagonal; in fact $i\hbar 1$.

[flashback: if A + B are hermitian, $(AB)_{mn} = \sum_l a_{ml} b_{ln}$

$(AB)^*_{mn} = \sum_l a^*_{ml} b^*_{ln} = \sum a_{lm} b_{nl}$

$= (BA)_{nl}$

$\therefore \widetilde{AB}^* = BA$

$\therefore AB$ in general not Hermitian

$\therefore xp$ not Hermitian,

for $\widetilde{xp}^* = px \neq xp$.

but $(\widetilde{xp+px})^* = (px+xp) = xp+px$, $\therefore$ Hermitian

$\therefore$ if A + B are Hermitian,

$\frac{1}{2}(AB+BA)$ is Hermitian.

"symmetrical product".

Used to be important to "symmetrize" the Hamiltonian

Since Hamiltonian must be Hermitian.

[only Hermitian operators have real eigenvalues].

[can be shown that roots ε of $\|A - \varepsilon 1\| = 0$

are real only if $A_{nm} = A^*_{mn}$.]

All dynamical quantities must be represented by Hermitian operators

first comm. $\{ \lambda^{\prime} p$

Oct 3 $\quad px - xp = -i\hbar$

(for corresponding coord's & mom.)

in: $\quad p_k x_l - x_l p_k = -i\hbar\, \delta_{kl}$ $\qquad k, l = 1, \dots 3n$ for n particles

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$$[p^2 x] = p[px] + [px]p = -2i\hbar\, p$$

$$[p^n x] = p^{n-1}[px] + [p^{n-1}x]p = -i\hbar\, p^{n-1} + [p^{n-1}x]p$$

$$(i\hbar\, p^{n-2} + [p^{n-2}x]p)p$$

$$i\hbar\, p^{n-1} + [p^{n-2}x]p^2$$

$$\therefore [p^n x] = -i\hbar\, n p^{n-1}$$

$$[f(p)\, x] = -i\hbar \frac{df}{dp}.$$

$$[p x^n] = -i\hbar\, n x^{n-1}$$

$$[p\, f(x)] = -i\hbar \frac{\partial f}{\partial x}.$$

$$[p^2 x^2] = p[px^2] + [px^2]p = -2i\hbar\,[px + xp]$$

$$[p^m x^n] = -n i\hbar\,[p^{m-1} x^{n-1} + p^{m-2} x^{n-1} p + \dots + x^{n-1} p^{m-1}]$$

$$[f(p)\, g(x)] = -i\hbar\,[S \frac{df}{dp} \frac{dg}{dx}.]$$ where S indicates symmetrized expression

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$$H_{mn} = \int \psi_m^* H \psi_n = E_n \delta_{mn}$$

Suppose we have a matrix A: calculate $(AH - HA)$

$$(AH - HA)_{mn} = (AH)_{mn} - (HA)_{mn} = \sum_l A_{ml} H_{ln} - \sum_l H_{ml} A_{ln}$$

$$= A_{mn} E_n - E_m A_{mn}$$

$$= A_{mn}(E_n - E_m)$$

If A is also diagonal : $A_{mn} = A_m \delta_{mn}$

$$(AH - HA)_{mn} = (E_n - E_m) A_{mn} = (E_n - E_m) A_m \delta_{mn}$$

$$\equiv 0 .$$

<u>Two diagonal matrices commute</u>

A diagonal matrix H commutes ~~with~~ a matrix A if A_{mn} vanishes for states for which $E_m \neq E_n$

e.g.: if $H = \begin{pmatrix} E^1 & & & \\ & E^1 \ddots & & \\ & & E^2 \ddots & \\ & & & E^3 \ddots \end{pmatrix}$ $\quad A = \begin{pmatrix} \ddots & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \ddots \end{pmatrix}$ etc

A commutes with H if $A_{mn} \neq 0$ only in squares.

Now $A_{mn} = \int \psi_m^* A \psi_n = \int u_m^* A u_n \, e^{\frac{i}{\hbar}(E_m - E_n)} = \alpha_{mn} e^{\frac{i}{\hbar}(E_m - E_n)}$

α_{mn} independent of t

Now $\dfrac{dA_{mn}}{dt} = \dfrac{i}{\hbar}(E_m - E_n) A_{mn} = -\dfrac{i}{\hbar}(AH - HA)_{mn}$

$$\therefore \quad \frac{dA}{dt} = -\frac{i}{\hbar}(AH - HA) = -\frac{i}{\hbar}[AH] .$$

if $A = H$, $\dfrac{dH}{dt} = 0$

Suppose $\psi = \sum c_n \psi_n$

then av $A = \int \psi^* A \psi = \int \sum c_m^* \psi_m^* A \sum c_n^* \psi_n = \sum_{m,n} c_m^* c_n A_{mn}$

$$\text{av } \frac{dA}{dt} = \sum_{mn} c_m^* c_n \frac{dA_{mn}}{dt}$$

$$\frac{dx}{dt} = -\frac{i}{\hbar}[xH] \qquad H = H(x,p) = V(x) + T(p) \quad \text{in multi cases.}$$

$$\therefore \frac{dx}{dt} = \frac{i}{\hbar}[x, T(p)] = -\frac{i}{\hbar}\cdot i\hbar\frac{dT}{dp} = \frac{dT}{dp} = \frac{\partial H}{\partial p}$$

$$\dot{x} = \frac{\partial H}{\partial p}$$

$$\frac{dp}{dt} = \frac{i}{\hbar}[pH] = -\frac{i}{\hbar}[pV] = -\frac{i}{\hbar}\cdot -i\hbar\frac{\partial V}{\partial x} = -\frac{\partial V}{\partial x} = -\frac{\partial H}{\partial x}$$

$$\therefore \dot{p} = -\frac{\partial H}{\partial x}$$

which are the classical Hamilton eq'n's. !

Hence in Q.M., $\frac{dA}{dt} = -\frac{i}{\hbar}[AH]$ is called eq'n of motion.

Derive Ham. eqns from Schroedinger eq'n.

10/5/40 $[p,x] = -i\hbar$

$$\frac{dA}{dt} = -\frac{i}{\hbar}[A,H], \text{ where } \begin{cases} \frac{\partial x}{\partial t} = \frac{\partial H}{\partial p} \\ \frac{\partial p}{\partial t} = -\frac{\partial H}{\partial x} \end{cases}$$

center of gravity of wave packet moves according to Ham eq., i.e. classical mech

Transition to classical mechanics.

Classical Mechanics applicable if a wave packet can be constructed over which the force does not vary appreciably.

Extension of wavepacket $\cdot \frac{\partial H}{\partial p} = \frac{\partial}{\partial p}$

Variation of force over one wave length must be small.

Bohr correspondence principle: in limit of high quantum no.'s, can use classical mechanics; in particular, can calculate radiation.

For high q. n.'s, get nearly equidistant energy levels.

$$x_{mn} = x^0_{mn}\, e^{\frac{i}{\hbar}(E_m - E_n)}$$

for equidistant levels: $x_{mn} = x^0_{mn}\, e^{\frac{i}{\hbar}\frac{dE}{dn}(m-n)}$

$$= x^0_{mn}\, e^{i\omega_0 t(m-n)}$$

$$\psi = \sum c_n \psi_n$$

suppose we construct a ψ with concentration of ψ_n's about n.

It will be about at the n's orbit in Bohr theory.

higher x_{mn}'s correspond to classical Fourier components of x, from which radiation, etc. are calculated. : emitted radiation $\sim |x_{mn}|^2 \omega^4$

$\omega = \omega_0(m-n)$

Heisenberg devised a scheme which gave correspondence between high q. n.'s & classical mech.

Derived commutation relation so as to give quantum condition

Transition probabilities - $nl \to n'l'$ strong if n, l change in same direction

weak " " " " opposite "

if $l \approx n$, trans. prob. for large Δn is very small.

if $l \ll n$, " " decreases slowly with inc. Δn

[if $l \approx n$, almost circular orbit; then cont. x is nearly $\sin n$, ~~contains only~~ &

Fourier coeff of all but ω_0 vanish; but eccentric orbit will contain many

Harmonic oscillator by Dirac's method.

$$H = p^2 + \frac{m\omega^2}{2} x^2$$

$$\dot{x} = \frac{\partial H}{\partial p} = p/m \qquad \therefore\ m\dot{x}_{mn} = p_{mn}$$

$$\dot{p} = -\frac{\partial H}{\partial x} = -m\omega^2 x \qquad \dot{p}_{mn} = -m\omega^2 x_{mn}$$

$$\left[\ \ddot{p}_{mn} = -\omega^2 p_{mn},\right.$$

$$p_{mn} = m\dot{x}_{mn} = m \cdot \frac{i}{\hbar}\left[xH - Hx\right]_{mn} \qquad \ddot{x}_{mn} = -\omega^2 x_{mn}$$

$$= -\frac{im}{\hbar} x_{mn}\left[E_n - E_m\right] \qquad x_{mn} = -\frac{1}{m\omega^2}\dot{p}_{mn} = +\frac{i}{m\omega^2\hbar}\left[pH - Hp\right]$$

$$= \frac{i}{m\omega^2\hbar} p_{mn}(E_n -$$

$$\therefore\ p_{mn} = -\frac{im}{\hbar}\left[E_n - E_m\right]\frac{i}{m\omega^2\hbar} p_{mn}(E_n - E_m) = \frac{1}{\omega^2\hbar^2}(E_n - E_m)$$

and $x_{mn} = \frac{i}{m\omega^2\hbar}(E_n - E_m)\left[-\frac{im}{\hbar}(E_n - E_m)x_{mn}\right] = \frac{1}{\omega^2\hbar^2}(E_n - E_m)$

$\therefore\ x_{mn}, p_{mn}, \neq 0$ only if $(E_n - E_m)^2 = \hbar^2\omega^2$

$E_n - E_m = \pm\hbar\omega$

otherwise, $x_{mn} = 0$.

$\therefore$ matrix elements exist only between states whose energy difference is $+\hbar\omega$.

Sect. 8] p_{mn}

$$\therefore\ x_{mn} = x^0_{mn}\, e^{i\hbar^{-1}(E_n - E_m)t} = x^0_{mn}\, e^{\pm i\omega t}$$

$\therefore$ all matrix elements have classical vibration frequency

If there is a level E_n, ~~then~~ are levels $E_n \pm \omega\hbar$; ~~same~~ $E_n \pm 2\omega\hbar$

$\therefore$ levels are given by $E_n = \hbar\omega(\alpha + n)$ α a constant

(so far, might have several α's, hence several series).

Now consider energy matrix elements.

$$E_n = H_{nn} \qquad H_{nn} = \frac{1}{m}\sum_l p_{nl}\, p_{ln} + \frac{1}{2} m\omega^2 \sum_l x_{nl}\, x_{ln}$$

$$= \sum_m p_{nm}\, p_{mn}$$

$$= 0 \text{ unless } m = n.$$

$$= p_{nn}\, p_{nn}$$

$$E_n = H_{nn} = \frac{1}{2m}\left(p_{n,n+1}\, p_{n+1,n} + p_{n,n-1}\, p_{n-1,n}\right)$$

$$+ \frac{1}{2} m\omega^2 \left(x_{n,n+1}\, x_{n+1,n} + x_{n,n-1}\, x_{n-1,n}\right)$$

$$= \frac{m}{2\hbar^2}(E_n - E_l)^2\, x_{nl}\, x_{ln} + \frac{1}{2} m\omega^2\, x_{nl}\, x_{ln}$$

$$= \left(\frac{1}{2} m\omega^2 + \frac{1}{2} m\omega^2\right) \sum_l x_{nl}\, x_{ln}$$

$$= m\omega^2 \sum x_{nl}\, x_{ln}^* \qquad (\text{since } x \text{ is real})$$

$$= m\omega^2 \left[\, |x_{n,n-1}|^2 + |x_{n,n+1}|^2 \,\right]$$

$$= \hbar\omega(\alpha + n)$$

$$\therefore\ |x_{n,n-1}|^2 + |x_{n,n+1}|^2 = \frac{\hbar}{m\omega}(n + \alpha)$$

$$\text{also } |x_{n+1,n}|^2 + |x_{n+2,n+1}|^2 = \frac{\hbar}{m\omega}(n + 1 + \alpha)$$

$$\therefore\ |x_{n+2,n+1}|^2 - |x_{n,n-1}|^2 = \frac{\hbar}{m\omega}$$

$$\therefore\ |x_{n-1,n}|^2 = \frac{\hbar}{m\omega}(n + \beta)$$

$$\therefore\ \frac{\hbar}{2m\omega}\left((n+\alpha) + (n+1+\alpha)\right) = \frac{\hbar}{m\omega}(n + \alpha)$$

$$\therefore\ n + \alpha + \tfrac{1}{2} = n + \alpha;$$

$$\therefore\ \alpha = \beta + \tfrac{1}{2}$$

Now $|x_{n,n-1}|^2$ must be positive; hence the

must be a smallest value of n for which the matrix element exists, since there can be no lowest energy level E_0. Hence there exists no $|x_{0,-1}|$;

$$\therefore \quad |x_{0,1}|^2 = \frac{\hbar}{m\omega}\alpha ;$$

$$\text{also} \quad |x_{-1,0}|^2 = 0 = \frac{\hbar}{2m\omega}(0+\alpha)$$

$$\therefore \alpha = 0, \quad \alpha = 1$$

$$\text{and} \quad E_n = \omega\hbar(n+\tfrac{1}{2}) \qquad n = 0, 1, \ldots$$

$$x_{n-1,n} = \sqrt{\frac{\hbar n}{2m\omega}}\, e^{i\gamma_n}$$

γ_n is arbitrary (just as in wave mech, such wave fn is arbitrary to a phase factor).

This theory gives all the following, they give a single, unique element in a definite way. If ψ is more complicated, multiply matrix

$$E = \begin{pmatrix} 1 & & & & \\ & 2 & & & \\ & & 3 & & \\ & & & 2 & \\ & & & & 5/2 \\ & & & & & \ddots \end{pmatrix}\hbar\omega \qquad x = \begin{pmatrix} 0 & 1 & & & \\ 1 & 0 & \sqrt{2} & & \\ & \sqrt{2} & 0 & \sqrt{3} & \\ & & \sqrt{3} & 0 & \sqrt{4} \\ & & & \sqrt{4} & \ddots \end{pmatrix}\sqrt{\frac{\hbar}{2m\omega}} \quad (\gamma_n = 0)$$

$$p = \begin{pmatrix} 0 & i & & & \\ i & 0 & -i\sqrt{2} & & \\ & i\sqrt{2} & 0 & -i\sqrt{3} & \\ & & i\sqrt{3} & 0 & -i\sqrt{4} \\ & & & i\sqrt{4} & 0 \\ & & & & & \ddots \end{pmatrix}\sqrt{\frac{1}{2}\hbar m\omega}$$

$x^2 + p^2$ have elements in main diagonal and 2nd diagonal away: the main diagonals add, + the rest cancel, to make E diagonal

Angular momentum.

(e particle).

$$\underline{M} = r \times p$$

$$M_3 = x p_y - y p_x \quad \text{etc.}$$

$$[z, M_3] = 0 = [p_z, M_3]$$

$$[x, M_3] = [x, x p_y] - [x, y p_x] = x[x, p_y] - [x, p_y]x - x[y, p_x] - [x, p_x]y$$

$$= -i\hbar y.$$

$$[z, M_x] = i\hbar y \quad \text{etc.}$$

$$[p_x, M_3] = [p_x, x]p_y = -i\hbar p_y.$$

$$[p_z, M_x] = i\hbar y \quad \text{etc.}$$

$$[r^2, M_3] = [x^2+y^2+z^2, M_3]$$

$$= [x^2, M_3] + [y^2, M_3]$$

$$= x[x, M_3] + [x, M_3]x + y[y, M_3] + [y, M_3]y$$

$$= -2i\hbar xy + 2i\hbar xy = 0.$$

also $[f(r^2), \underline{M}] = 0$

$[f(p^2), \underline{M}] = 0$

Set. 10

$[f(r), \underline{M}] = 0$

$[g(p), \underline{M}] = 0$

$[H(p,r), \underline{M}] = 0$ if $H(p,r) = f(p) + f(r)$.

$\therefore$ M has matrix elements only between states of same energy.

true for $M_{x,y,z}$, $M^2_{x,y,z}$ also for M^2

Matrix of M^2 can be diagonalized by taking appropriate linear combinations of ψ's. If a matrix commutes with a diagonal matrix it can always be diagonalized by taking suitable linear comb. of ψ's belonging to one eigenvalue of ψ. ?

$$[M_2, M_x] = [M_2, yp_3 - zp_y] = [M_2, y]p_3 - [M_2, z]p_y$$

$$= y[M_3 p_3] + [M_3, y]p_3 - z[M_3 p_y] - [M_3, z]p_y$$

$$= -i\hbar\,[\cancel{x}\,p_3 - \cancel{y}\,z\,p_x]$$

$$= -i\hbar\, M_y \quad \text{etc.}$$

$$\underline{M} \times \underline{M} = -i\hbar\, \underline{M}$$

also $[\underline{M}, M^2] = 0$.

Suppose each state corresponds to a definite value of E & M^2.

then $M_{x,y,z}$ have matrix elements only between states of the same E & M^2.

Suppose U_3 is also diagonal.

then U_x & U_y must be off-diagonal

~~$[U_x, U_y]_{mn} =$~~

$$[U_z, U_x]_{mn} = (U_{z;m} - U_{z;n}) U_{x;mn} = i\hbar\, U_{y;mn}$$

$$[U_z, U_y]_{mn} = (U_{z;m} - U_{z;n}) U_{y;mn} = -i\hbar\, U_{x;mn}$$

$$\therefore \quad (U_{z;m} - U_{z;n})^2 U_{x;mn} = \hbar^2 U_{x;mn}$$

$$\therefore \quad U_{x;mn} \neq 0 \text{ only if } U_{z;m} - U_{z;n} = \pm\hbar$$

$\therefore$ eigenvalues : $U_{z;m} = \hbar(m + \alpha)$

$$U_{y;m(m+1)}(-\hbar) = -i\hbar\, U_{x;m(m+1)}$$

$$U_{y;m(m-1)}(\hbar) = i\hbar\, U_{x;m,m-1)}$$

$$\therefore \quad (U_y - iU_x)_{m,m+1} = 0$$

$$(U_y + iU_x)_{m,m-1} = 0$$

$$[U_x U_y]_{mm} = U_{x;m,m+1} U_{y;m+1,m} + U_{x;m,m-1} U_{y;m-1,m}$$

$$- U_{y;m,m+1} U_{x;m+1,m} - U_{y;m,m-1} U_{x;m-1,m}$$

$$= -iU_{x;m,m+1} U_{x;m+1,m} + iU_{x;m,m-1} U_{x;m-1,m}$$

$$+ iU_{x;m,m+1} U_{x;m+1,m} + iU_{x;m,m-1} U_{x;m-1,m}$$

$$= 2iU_{x;m,m-1} U_{x;m-1,m} - 2iU_{x;m,m+1} U_{x;m+1,m}$$

Since M's are Hermitian matrices:

$$[M_x, M_y]_{mm} = 2i\{|M_{x;\,m-1,m}|^2 - |M_{x;\,m,m+1}|^2\}$$

but $[M_x, M_y]_{mm} = i\hbar M_{z;\,mm} = i\hbar(m\hbar)$ (from matrix multiplication)

$$= i\hbar^2 m$$

$$\therefore |M_{x;\,m-1,m}|^2 - |M_{x;\,m,m+1}|^2 = \frac{m\hbar^2}{2}.$$

$$\therefore |M_{x;\,m,m+1}|^2 = \hbar^2(\alpha + \beta m + \gamma m^2)$$

$$|M_{x;\,m-1,m}|^2 = \hbar^2(\alpha + \beta(m-1) + \gamma(m^2 - m + 1)$$

$$\text{diff.} = \hbar^2\{-\beta - 2\gamma m + \gamma\} = m\hbar^2$$

$$\therefore \beta = \gamma; \quad -2\gamma = 1$$

$$\gamma = -\tfrac{1}{2}$$

$$\therefore |M_{x;\,m,m+1}|^2 = \hbar^2(\alpha - \tfrac{1}{2}m - \tfrac{1}{2}m^2)$$

$$= \frac{\hbar^2}{2}(\alpha' - m(m+1))$$

$$|M^2|_{mm} = M^2_{x;\,mm} + \cdots$$

$$= M_{x;\,m,m+1}M_{x;\,m+1,m} + M_{x;\,m,m-1}M_{x;\,m-1,m} + \cdots \quad (3)$$

but $M^2_{y\,mm} =$

$$= \frac{\hbar^2}{4}\left(\alpha' - (m)(m+1) + \alpha' - m(m-1)\right) + \text{same} + m^2\hbar^2$$

$$= \hbar^2(\alpha' - m^2 + m^2 - m + m) = \alpha'\hbar^2$$

Suppose that existing state has $m = l$; then $M_{x;\,l,l+1} = 0$,

$\alpha' = l(l+1)$

then $M_x = 0$ also when $m = -l-1$

m goes from $-l$ to $+l$

and $M^2 = \hbar^2(l)(l+1)$.

Eigenvalues of $\mathcal{M}^2$: $l(l+1)\hbar^2$

of $\mathcal{M}_z$: $m\hbar = -l, -l+1 \ldots\ldots l-1, l \cdot \hbar$ $\quad 2l+1$ values of m

matrix elements of $\mathcal{M}_x$ exist only between states of same l, m differing by 1

l may be integral or half-integral. $\min 2l+1 = m$

By considering $x_p y - y_p x$, etc. can show that for orbital momentum, l must be integral (cf. Dirac).

[in wave mech, l is order of sph. harm., which must be integral if sph. harm. is single valued]

Notice that if $\mathcal{M}_z = \pm l$, $\mathcal{M}_z^2 = l^2$, but $\mathcal{M}^2 = l(l+1)$;

(here $\mathcal{M}_x^2 + \mathcal{M}_y^2 = \hbar^2 l$).

so simple vector model is dangerous.

We found $\mathcal{M}_{x;m,m+1} = \hbar \sqrt{l(l+1) - m(m+1)}$

or $\sqrt{(l-m)(l+m+1)}$

Often convenient to use: $\mathcal{M}_x \pm i\mathcal{M}_y$

these have elements: $\begin{pmatrix} & \times & & & \\ \times & & \times & & \\ & \times & & \times & \\ & & \times & & \ddots \\ & & & \ddots & \end{pmatrix}$ $\mathcal{M}_x + i\mathcal{M}_y$

$\begin{pmatrix} & \times & & & \\ \times & & \times & & \\ & \times & & \times & \\ & & \times & & \ddots \\ & & & \ddots & \end{pmatrix}$ $\mathcal{M}_x - i\mathcal{M}_y$

(These are Non-Hermitian operators)

(using usual sph. harm's, $\mathcal{M}_{x:\,m,m+1}$ has negative sign!)

Many-electron problem —

Potential energy V contains ~~term~~ $f(r_i)\ g(r_{ik})$.

$[\underline{M}_i, r_i] = 0$

also $[M_i, r_k] = 0$

But $[\underline{M}_{x_i}, r_{ik}^2] = [M_{x_i}, (x_i - x_k)^2 + \cdots\cdots]$

$= 0 + [M_{x_i}(y_i - y_k)^2] + [M_{x_i}(z_i - z_k)^2]$

$= -2[M_{x_i}, y_i y_k] - 2[M_{x_i}, z_i z_k]$.

$= -2[i\hbar z_i y_k - i\hbar y_i z_k]$

$= +2i\hbar[y_i z_k - z_i y_k]$

or: $[\underline{M}_i, r_{ik}^2] = 2i\hbar\ \underline{r}_i \times \underline{r}_k$

also $[\underline{M}_k, r_{ik}^2] = 2i\hbar\ \underline{r}_k \times \underline{r}_i$

Hence $[\underline{M}_i + \underline{M}_k, r_{ik}^2] = 0$

Hence sum of momenta of a pair of electrons commutes with relative position vector, & functions of it.

Also ~~total~~ orbital momentum $\underline{M} = \sum_k \underline{M}_k$ commutes with Hamiltonian (i.e. with all electron-interactions).

$[M_{x_1}, M_{y_1}] = i\hbar M_{z_1}$, etc.

Total mom. has same com. relations as single one.

$\therefore\ M^2 = \hbar^2(L+1)L$ $\qquad$ M, L, integers.

$M_z = \hbar M$. $M = -L \cdots\cdots L$

Spin. Pauli – correct to v^2/c^2.

1st approximation to Dirac eqn.

Each electron has intrinsic angular momentum: quantum no. $1/2$.

Computing spin $S_{x,y,z}$; $S_x S_y - S_y S_x = i\hbar S_z$ etc. just like ang mom

$$[S_{x,y,z}, S^2] = 0$$

$$[S_{x,y,z}, f(r)\, g(p)] = 0 .$$

If spin depends on new coordinate.

$$S^2 = \hbar^2 (s)(s+1)$$

$$S_z = \hbar \mu, \quad \mu = -s, \cdots +s .$$

For one electron: apparently, $s = 1/2$ (always)

$$\therefore S_z = -1/2, \ 1/2 ;$$

$$\therefore \quad S_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \hbar$$

$$S_{x:\mu,\mu+1} = \tfrac{1}{2}\hbar \sqrt{(s-\mu)(s+\mu+1)} = \begin{cases} \tfrac{1}{2}\hbar, & \mu = -\tfrac{1}{2} \\ \end{cases}$$

$$\therefore S_x = \hbar \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}$$

$$\text{also } S_y = \hbar \begin{pmatrix} 0 & -\tfrac{1}{2} i \\ \tfrac{1}{2} i & \end{pmatrix} .$$

use notation Pauli matrices: $\sigma = \dfrac{S}{\hbar/2}$.

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} .$$

$\boxed{\text{Show } [S_x S_y] = i\hbar S_z \text{ find } S^2 ;}$

I interaction of spin & orbit.

assume $\sim f(r)\, \underline{M} \cdot \underline{S}$.

$$[M_x, \underline{M}\cdot\underline{S}] = [M_x, M_x S_x] + [M_x, M_y S_y] + [M_x, M_z S_z]$$

$$= [M_x, M_y] S_y + [M_x, M_z] S_z = i\hbar [M_z S_y - M_y S_z]$$

$$= \cancel{\hbar}$$

also $[S_x, \underline{M}\cdot\underline{S}] = -i\hbar[M_3 S_1 - M_1 S_3]$.

$\therefore [M_x + S_x, M\cdot S] = 0$.

Prove: $[M^2, \underline{M}\cdot\underline{S}] = 0$

$\therefore$ also $[(\underline{M}+\underline{S})^2, \underline{M}\cdot\underline{S}] = 0$.

hence $[M^2+S^2, M\cdot S] = 0$.

also $[M^2, M\cdot S] = 0$

$[S^2, M\cdot S] = 0$

$2M\cdot S = (M+S)^2 - M^2 - S^2$

everything said above about ang. mom. holds for $\underline{M}+\underline{S}$

$(M+S)^2 = \hbar^2 j(j+1)$

$\therefore 2M\cdot S = \hbar^2[j(j+1) - l(l+1) - s(s+1)]$.

Can also introduce total ang. mom of many electrons;

$J = \underline{M}+\underline{S} = \sum_l M_l + \sum_l S_l$

$[J, f(q_l, p_l)] = 0$

also $[J, M+S] = 0$;

$\therefore J$ commutes with whole Hamiltonian & is a time quantity

[illegible] p. [illegible] ang. mom. [illegible]

$[M_x T_x] = 0$ $\quad$ T_x, x — p. / [illegible] $\underline{\text{ang. mom.}}$ $\underline{\text{ang. mom.}}$ $\underline{M}$

$[M_x T_y] = i\hbar T_z$

also if i is total ang. mom. [illegible] to

also:

$[\underline{M}, T_1 \cdot T_2] = 0$ $\quad$ on T is r_i for ith [illegible]

on S_i for [illegible]

for $[M_x, T_1 T_2] = [M_x, T_1] \cdot T_2 + T_1 [M_x, T_2]$

$= i\hbar \{ T_{1z} T_{2y} - T_{1y} T_{2z} + T_{1y} T_{2z} - T_{1z} T_{2y} \} = 0$

[illegible] product [illegible] the [illegible] in [illegible] to [illegible] mom.

M commutes with $L_i S_i$, with $r_i \cdot p_i$ for single electron.

[illegible] of [illegible] in [illegible] [illegible] to [illegible]

is given by $Z_{mn} = (m|z|n) = (E l m | z | E' l' m')$

[illegible] or for [illegible] system: $(E J M | z | E' J' M')$

this vanishes for $M' \neq M$, since z commutes with M_z which is diagonal.

$(E J M | \underset{y}{x} | E' J M') \neq 0$ if $|M - M'| = 1$

Assume $J' = J$; then

$(E J M | [x M_z] | E' J' M') = (E J M | x | E' J M')(M' - M)\hbar$

$= -i\hbar (\cdots | y | \cdots)$

For state [illegible] same J: $(E J M | x | E' J' M') = \delta_{J, E E'} (\# J M | M_x | J M')$

$|z|$ $\quad$ $\alpha \ldots (\cdots | M_z | \cdots)$

$|(\cdots|x|\cdots)|^2$ gives intensity of Zeeman component of line –

J selection rule

$[M^2, J] =$ —

$[M^2, [M^2, J]]$ depends on $J + M_J$ C. S.

$= M^4 J - 2M^2 J M^2 + J M^4$

$= 2\hbar^2 [M^2 J + J M^2 - 2 M_J \hbar \cdot \pm]$

Transition $J \to J'$ possible –

$E\, J M | \cdots | E' J' M' | = (\cdots|J|\cdots)\{J^2(J+1)^2 - 2J(J+1)J'(J'+1) + J'^2(J'+1)^2\}$
$- 2\hbar^2 (J(J+1) + J'(J'+1))$

$= - - \{[(J-J')^2 - 1][(J+J'+1)^2 + 1]\} = 0$

$\therefore$ (– 1 3 +) to unless.

$(J - J')^2 - 1 = 0$

or $J - J' = \pm 1$

Parity must change in dipole transition

Read Pauli + Schiff !

Transformation Theory.

Problem: find some function such that any given observable is represented by a diagonal matrix. These ~~matrix~~ matrices will not have the same simple ~~[illegible]~~ definition as previously.

Theory of transformations from one system of axes to another, in which different observables are diagonal.

These transformations are a choice of new axes in ~~Hilbert~~ the space.

Oct 17 | In three dimensions:

New coordinates of a vector after a mapping A:

$$y_m = \sum A_{mn} x_n .$$

Then ask whether can find a new set of axes x' ~~such that~~

$$x_n = \sum S_{ni} x_i'$$

$$x = S x'$$

Define $S^{-1}S = 1$, then $S^{-1} x = x'$.

must have $\sum |x_n|^2 = \sum |x_n'|^2$;

from this, must have $S \tilde{S}^* = I$

or $S^{-1} = \tilde{S}^*$.

then $y_m = \sum S_{mk} y_k' = \sum_n \sum_i A_{mn} S_{ni} x_i'$

Now want to transform to principal axes – i.e. $y_k' = \lambda_k x_k'$

the equations coefficients: $S_{mk} \lambda_k = \sum_n A_{mn} S_{nk}$ for each k m

This gives 9 equations for the nine S_{ij}'s.

solution if det. of coefficients vanishes: $\| A_{mn} - \lambda_k \delta_{mn} \| = 0$

This gives ratios of S_{ij}'s – normalize by unitary requirement $\sum S^{*}_{ni} S_{ni} = 1$

$$\sum_n |S_{nk}|^2 = 1 \qquad \sum S_{nk} S^{*}_{ni} = 0 \text{ if } k \neq i .$$

Hilbert space:

coordinates are expansion coefficients of a ψ with respect to a set of eigenf'ns ψ_n.

$$\psi = \sum_n c_n \psi_n .$$

c's like x's

b's like y's.

Suppose $A\psi = \sum_n b_n \psi_n$

$$= \sum_n c_n A \psi_n$$

$$= \sum_n c_n \sum_m A_{mn} \psi_m$$

$$A_{mn} = \int \psi_m^{*} A \psi_n$$

A_{mn} like A_{mn}

where $b_m = \sum_n A_{mn} c_n$

Can we introduce a new system of axes? – (i.e. a new set of basic eigenf'ns) such that $A\psi$ is represented by a diagonal matrix?

Suppose we have a system of eigenf'ns ψ_n'.

Then $\psi = \sum_n c_n' \psi_n'$

$$c_m = \sum_n S_{mn} c_n'$$

$$\therefore \psi = \sum_m \sum_n S_{mn} c_n' \psi_m = \sum_n c_n' \psi_n'$$

$$\therefore \psi_n' = \sum_m S_{mn} \psi_m$$

& we have relation between ψ's

$$b_m = \sum_l S_{ml} b_l'$$

$$= \sum_n A_{mn} c_n = \sum_n \sum_l A_{mn} S_{nl} c_l'$$

For diagonalization : $b_k' = \lambda_k c_k'$.

$$\therefore \; S_{mk}\lambda_k = \sum_n A_{mn} S_{nk}$$

Same as before – but infinite no of eqns for each k,

solved if $\quad |A_{mn} - \lambda_k \delta_{mn}| = 0$.

Solvable if A_{mn} has certain properties . .

λ_k's are called eigenvalues of A .

and ψ_k' is k^{th} eigenfunction of A .

$$\text{and} \quad A\psi_k' = \lambda_k \psi_k' -$$

$$\text{For} \quad A\psi = \sum_i b_i' \psi_i'$$

$$\left.\begin{aligned} &= \sum \lambda_i c_i' \psi_i' \\ &= \sum c_i' A\psi_i' \end{aligned}\right\} \text{ equate coefficients}$$

In elementary Q.M., energy function usually constant;

In primed representation, A is diagonal : $A_{ik}' = \int \psi_i'^* A \psi_k'$

$$= \int \psi_i'^* \psi_k' = \lambda_k \delta_{ik} .$$

If a diagonal matrix is Hermitian,

must be real, for must have $A_{ik}' = A_{ki}'^*$

or $\lambda_k = \lambda_k^*$, $\therefore \lambda_k$ real .

Is A' Hermitian, if A was ?

$$\text{Now} \quad S_{mk}\lambda_k = \sum A_{mn} S_{nk}$$

$$\text{or} \quad S A' = A S$$

$$\text{where } A' = S^{-1} A S$$

$$\therefore A'_{ik} = \sum S^{-1}_{in} \sum A_{mn} S_{mk} \qquad \text{but } S^{-1}_{in} = S_{ni}^*$$

$$\therefore \quad A'_{ik} = \sum_{mn} A_{mn} S^*_{mi} S_{nk}$$

$$A'^*_{ki} = \sum_{mn} A_{mn} S^*_{mk} S_{ni} = \sum_{mn} A^*_{mn} S^*_{nk} S_{mi}$$

$$\therefore \quad \cancel{A'^*_{ki} = \sum_{mn} A^*_{mn} S^*_{mk} S_{ni} = \sum_{mn} A_{mn}}$$

$$\therefore A'_{ki} = \sum_{mn} A^*_{mn} S^*_{nk} S_{mi} = A'^*_{ik}$$

(since A is Hermitian)

$\therefore$ if $\left\{ \begin{array}{l} A \text{ is Hermitian,} \\ \text{and } S \text{ unitary} \end{array} \right\}$, A' also is.

Ex. 19

$$\Psi = \sum_m c_m \psi_m = \sum_m c'_m \psi'_m$$

where $c_m = \sum_k S_{mk} c'_k$

Whence $\psi'_k = \sum S_{nk} \psi_n$

$$A\psi = \sum_n b_n \psi_n \quad , \quad b_n = \sum_m A_{nm} c_m$$

$$A\psi' = \sum_k b'_k \psi'_k \quad , \quad b'_k = \lambda_k c'_k$$

$$S_{mk} \lambda_k = \sum_n A_{mn} S_{nk}$$

S determining then solve $\| A_{mn} - \lambda_k S_{mn} \| = 0$

+ get eigenvalues λ_k.

Now $\left[\begin{array}{l} S^*_{mk} \lambda^*_i = \sum_n A^*_{mn} S^*_{nk} \\ S_{mi} \lambda_i = \sum_n A_{mn} S_{ni} \end{array} \right| \begin{array}{l} S_{mi} \\ S^*_{mk} \end{array} \left| \begin{array}{l} \sum_m \\ \sum_m \end{array} \right.$

$$\text{Hence} \quad \lambda^*_i \lambda_i \sum_m S^*_{mk} S_{mi} = \sum A^*_{mn} S^*_{nk} \sum A_{mn} S_{ni}$$

But t is Hermitian; $t_{mn} = A^*_{nm}$.

therefore $(\lambda_i^* - \lambda_k) \sum_n S^*_{ni} S_{nk} = 0$

either $\lambda_i^* = \lambda_k$

or $\sum_m S^*_{mi} S_{mk} = 0$.

~~hence~~

Hence $\int \psi_i^* \psi_k = \int \sum S^*_{mi} \psi^*_m \sum S_{nk} \psi_n$

$= \sum_{mn} S^*_{mi} S_{nk} \int \psi_m^* \psi_n$ (ψ's are orthogonal)

$= \sum_m S^*_{mi} S_{mk} = 0$

Hence new ψs, ψ' are ~~orthogonal~~.

If $\lambda_i^* = \lambda_k$, $\sum S^*_{mi} S_{mk} \neq 0$; hence for degenerate states ψ's not orthogonal. (But we can take linear combinations that are orthogonal).

Suppose we have degenerate states:

$$A\psi'_{kj} = \lambda_k \psi'_{kj}$$

can take $\psi_k = \sum a_j \psi'_{kj}$ + make them orthogonal

---

Reality properties:

$$\lambda_k \underbrace{\sum_m S_{mk} S^*_{mk}}_{\text{real}} = \underbrace{\sum_{mn} t_{mn} S_{nk} S^*_{mk}}_{\text{real}} \quad \therefore \lambda_k \text{ real.}$$

∴ if two eigenvalues are equal eigenfunctions are orthogonal. If they are equal can be made orthogonal.

$$\int \psi_k'^* \psi_l' = \sum_n S_{nk}^* S_{nl} = 1 \quad \text{for normalization.}$$

but if $\sum_i S_{ni}^* S_{in} = \delta_{nl}$, S is unitary.

i.e. $S^{-1} = S^*$.

But if S is unitary S^{-1} is also unitary, so changes primed fns. to unprimed fns.

$$\psi_n = \sum_k S^{-1}_{kn} \psi_k \qquad \left[\text{for if } \psi_n = \sum_k T_{nk} \psi_k,\right.$$

$$\psi_n = \sum_k S_{nk} T_{jn} \psi_j$$

$$\therefore \sum_n T_{jn} S_{nk} = \delta_{jk}$$

$$\therefore T = 1$$

$$\therefore T = S^{-1} \left.\right]$$

also $c_k = \sum_n S^{-1}_{kn} c_n$

$$= \sum_n S^*_{kn} c_n$$

$$= \sum_n S^*_{nk} c_n$$

In usual notn, $S_{nk} = \int \psi_n^* \psi_k$

$$S^{-1}_{kn} = \int \psi_k'^* \psi_n = S^*_{nk}$$

If B is operator in unprimed system:

$B_{ik} = \int \psi_i'^* B \psi_k'$ it also is in new system.

Dirac Notation:

If suppose $\mathcal{C}$ is diagonal in ψ system; $\mathcal{T}$ is diagonal in ψ' system.

Let states by B_n Denote eigenstates by A_k

call transformation function $(B_n|A_k) = S_{nk}$

classical quantities are numbers - if is etc.

also write $C_n = (B_n|)$

$$\left(\text{i.e. } \psi = \sum (B_n|)\psi_n\right.$$

$(B_n|)$ are representations of state ψ

then $(B_n| \;) = \sum_k (B_n|A_k)(A_k|$

Can have matrices of these elements;

i.e. $(B_m|\mathcal{C}|B_n) = \int \psi_m \mathcal{C} \psi_n = \int \psi_m^* \mathcal{C} \psi_n$

also $(B_m|\mathcal{C}|B_n) = \sum (B_m|A_i)(A_i|\mathcal{C}|A_j)(A_j|B_n)$

[For $\psi_n = \sum_k (B_k|A_n)\psi_k'$?

$S^{-1}_{kn} = (A_k|B_n)$

$\psi_m^* = \sum_i (A_i|B_m)^* \psi_i'^*$

$(A_k|B_n) = (B_n|A_k)^*$]

matrix elements of C, in terms of eigenf'ns of A: $(A_i|C|A_k)$.

Transformation function $(A_k|B_n)$.

(Transform ortho in Hilbert space)

Expansion coefficients of w. state: $(A_k|)$ $\qquad \psi = \sum (A_k|)\psi_{A_k}$

then $(A_k|) = \sum (A_k|B_n)(B_n|)$ rel. of exp. coeff. of ab.

$\psi_{B_n} = \sum (A_k|B_n)\psi_{A_k}$ rel. of eigenf'ns.

$(B_n|A_k)\,A_k = \sum (B_n|A|B_m)(B_m|A_k)$ determines of transf.

$(A_k|B_n) = (B_n|A_k)^*$ (Unitary matrix).

and $(A_i|C|A_k) = \sum_{mn} (A_i|B_m)(B_m|C|B_n)(B_n|A_k)$.

Main purpose of transf. theory is to calculate matrix elements in a convenient system of wave f'ns.

Example: Spin-Orbit interaction $\sim \underline{S}\cdot\underline{L}$.

$S_{x,y,z}$ $L_{x,y,z}$ $J_{x,y,z}$, S^2, L^2, J^2.

A representation: (L_3, S_3) $L_3(\mu)\,S_3(\sigma)$. want to get $(L_3(\mu)S_3(\sigma)|L\cdot S|L_3(\mu')S_3($

B " : (J_3, J) $J_3 = L_3 + S_3$ This can be done.

$J^2 = L^2 + S^2 + 2L\cdot S$ but easier to get:

$(J_3(m)\,J^2(j)\,|L\cdot S|\,J_3(m')\,J^2(j)$

Now need $(A_k|B_n)$

which is here $(L_3(\mu)S_3(\sigma)|J_3(m)\,J^2(j,j+1)) = \delta_{m,\mu+\sigma}\,(L_3(\mu)S_3(m-\mu)|J_3(m)$

Hence for each m, ψ_{Bjm} contains at most $2s+1$ functions $\psi_{A\mu\sigma}$

$\sigma = -s \ldots\ldots +s$

$\mu = m-s \ldots\ldots m-$

$\sim s$

We need $(\mu\sigma|\vec{J}^2|\mu'\sigma')$

then $(\mu\sigma|mj)\, j(j+1) = \sum_{\mu'\sigma'} (\mu\sigma|\vec{J}^2|\mu'\sigma')(\mu'\sigma'|mj)$

Now $[\vec{J}_3, L\cdot S] = 0$

$[\vec{J}^2, L\cdot S] = 0$

$\therefore$ $L\cdot S$ matrix element vanishes unless $m = m'$; $j = j'$;

$\therefore$ $(mj|L\cdot S|m'j') = \delta_{mm'}\,\delta_{jj'}\left[\frac{1}{2}[j(j+1) - l(l+1) - s(s+1)]\right]$

(since $L\cdot S = \frac{1}{2}J^2 - L^2 - S^2$).

Then use transf. f'n to get matrix in μ, σ system.

---

largest $m = l+s$; $\mu = l$, $\sigma = s$

$(\mu\sigma|mj)\, j(j+1) = (\mu\sigma|\vec{J}^2|\mu\sigma)(\mu\sigma|mj)$

$\longrightarrow = l(l+1) + s(s+1) + 2ls$

$= (l+s)(l+s+1)$

next: $m = l+s-1$; $\begin{cases} \mu = l & \sigma = s-1 \\ \mu = l-1 & \sigma = s \end{cases}$

Here $(l, s-1|\vec{J}^2|l, s-1)$, same as above;

but $(l-1, s|\vec{J}^2|l, s-1)$, only $L_xS_x + L_yS_y$ give contribution;

$(l-1, s\ 2(L_xS_x + L_yS_y)\, l, s-1) = 2\sqrt{ls}$

etc.

(In this case, nothing novel -

Oct 24

Invariance of $\{\text{Spin}\}$ matrix $\quad \text{Spin} = \sum_k A_{kk}$.

Spin is invariant under unitary transformation.

$$A'_{kk} = \sum_{mn} S_{km} A_{mn} S^{-1}_{nk}$$

$$\text{Spin} = \sum_k A'_{kk} = \sum_{kmn} S_{km} A_{mn} S^{-1}_{nk}$$

$$= \sum_{mn} A_{mn} \sum_k S_{km} S^{-1}_{nk}$$

Principle of spin-orbit stability

$$= \sum_{mn} A_{mn} \delta_{mn}$$

$$= \sum_n A_{nn}$$

Eg: Transformation $\overset{L\,S}{\mu\sigma} \to \overset{A_3\,n^{-2}}{mj}$

$$(\mu, m-\mu \mid C \mid \mu', m-\mu')$$

$$(m, j \mid C \mid m, j')$$

$$\text{Spin}: \sum_\mu (\mu, m-\mu \mid C \mid \mu, m-\mu) = \sum_j (m, j \mid C \mid mj)$$

e.g. $\quad (\mu\sigma \mid L\cdot S \mid \mu\sigma) = \mu\sigma$

largest value: $m = l+s$, $\mu = l$, $\sigma = s$

$\mu\sigma = ls$.

and $ls = (j = l+s \mid L\cdot S \mid l+s)$

But $L\cdot S$ commutes w. L, J, S, J_3

$L\cdot S$ depends, for given $l+s$, on j, but not on m.

if $m = l+s-1$ $\quad \left.\begin{matrix}\mu = l-1 & \sigma = s \\ \mu = l & \sigma = s-1\end{matrix}\right\}$ $\quad \therefore (L\cdot S) = \begin{matrix} l(l-1)s \\ l\,s(s-1) \end{matrix}$

$\text{Sum} = 2sl - l - s$

Then in j rep., there are two states, one with $j = l+s$, $m = l+s-1$

& one other.

Then by orthogonality, we have;

$$\langle ls-l-s \rangle = (j\,l+s\,|\,\underline{L}\cdot\underline{S}\,|\,l+s) + (j'\,|\,\underline{L}\cdot\underline{S}\,|\,j')$$

$$= ls + (j'\,|\,\underline{L}\cdot\underline{S}\,|\,j')$$

$j' = l+s-1$

$$\therefore (j'\,|\,\underline{L}\cdot\underline{S}\,|\,j') = ls - l - s.$$

Keep this ~~racket~~ up until all j matrix elements are found

Method same. $j = l+s,\ l+s-1 \ldots\ldots |l-s|$.

---

80 Electrostatic interaction of electrons –

e.g. p^2 ^1S ^1D ^3P calculation by method of perturbation;

~~Take possible~~ 2 representation: μ_1, μ_2 and $\mu_1 + \mu_2$, & L

→ sph. harmonics $P_1^{\mu_1}(1)\, P_2^{\mu_2}(2)$.

Calculate $\frac{e^2}{r_{12}}$ matrix elements in μ_1, μ_2 rep;

then transform to $\mu_1 + \mu_2$, L rep. by taking largest value first:

$\mu = 2$, $\mu_1 = \mu_2 = 1$, $L = 2$ ^1D

then $\mu = 1$ $\mu_1 = 1$ $\mu_2 = 0$ $L = 2$

or $\mu_1 = 0$ $\mu_2 = 1$ $L = 1$ ^3P

Calculate ($|\frac{e^2}{r_{12}}|$) for these ↑, add them, multiply (diagonal) value for $L = 2$, & get value for $L = 1$.

Slater. P.R. 24 Then $\mu = 0$ $\mu_1 = 1$ $\mu_2 = -$ ~~$L = 1$~~

$\mu_1 = 0$ $\mu_2 = 0$

$\mu_1 = -1$ $\mu_2 = 1$ $L = 0$

Then $\mu = 0$ $L = 0$

In second case, $E = \frac{a^2}{1/2}$ matrix is of form: $\begin{pmatrix} a & b \\ b & a \end{pmatrix}$ $\begin{matrix} d_0 \\ d_1 \end{matrix}$

If diagonalized, eigenvalues are $a \pm b$,
eigenfn's are sum + diff of
original fn's.

(in fact, same for 1D state
diff. for 3P state).

^3P : $(1,-1) - (-1,1)$

Third case, ^1S : $(1,-1) + (-1,1) + 0,0$

^1D : $(1,1) + (-1,-1) - 2(0,0)$

Intermediate coupling. LS coupling. jj coupling.

individual l's make a result L
individual s's make a result S
valid if electrostatic interaction ≫ spin-orbit.
light atoms
^3P + ^3d cases of intermediate

individual j's add up.
spin-orbit ≫ electrostatic.
X-ray spectra
+ heavy elements often
satellites emitted
when atom is ionized
in two different planes —

Intermediate coupling prevails for outer shells of heavy elements. $Z > 30$ Neither approximation valid.

Spectroscopic ~~stability~~ helps: Take all levels given J; consider LS + jj representations; + consider matrix corresp. to given J; calculate diff. + sparks elements in each system. But this is more than necessary, for if you sum diagonal elements get same result in both

representations, from which we can get rest from spectrum.

By getting diagonal elements only, in all reps, we can calculate complete matrices –

Oct. 29 Method was used to find matrix elements in new representations –

Three representations A, B, C; A, B, C diagonal in each as respectively.

$(C_j|C|C_k) = \delta_{jk} C_k$ where C_k are eigenvalues.

$(A_l|C|A_m)$, $(B_n|C|B_p)$, can be found then to by looking for matrix elements:

$$\|(A_l|-|A_m) - \delta_{lm}\lambda\| = 0$$

$$\|(B_n|C|B_p) - \delta_{pn}\lambda\| = 0$$

algebraic eq'ns N^{th} rds for λ; must have same roots, hence same coefficients.

$\therefore$ can equate coefficients in two representations.

$$\begin{vmatrix} C_{11}-\lambda & C_{12} & C_{13} & \\ C_{21} & C_{22}-\lambda & C_{23} & \cdots \\ C_{31} & \cdots & \ddots & \\ \vdots & & & C_{NN}-\lambda \end{vmatrix} = (-1)^N\lambda^N + (-1)^{N-1}\lambda^{N-1}\sum_k C_{kk} + \cdots + \cdots + \|C_{ij}\| = 0$$

each coefficient invariant, hence space same in A, B, C rep

$\therefore \sum_l (A_l|C|A_l) = \sum_l (B_l|C|B_l) = \sum_k C_k$

Prove: invariance of determinant $\|A_{lm} - \delta_{lm}\lambda\|$ from unitary character of transformation

Take matrix of U_x in U_z representation and prove the invariance of exp + ~~[illegible]~~ $\langle\langle U_{z'}|U_x|U_{z'}\rangle\rangle$ for transf. to principal axes.

Repeated Transformations.

$$(A_k|) = \sum_m (A_k|B_m)(B_m|)$$

$$(A_k|C|A_l) = \sum_{mn} (A_k|B_m)(B_m|C|B_n)(B_n|A_l)$$

Sometimes want to transform from one to another rep. thru a third:

suppose I have $(D_p|)$ but not $(B_m|)$:

then $(A_k|) = \sum_{mp} (A_k|B_m)(B_m|D_p)(D_p|)$

then $(A_k|D_p) = \sum_m (A_k|B_m)(B_m|D_p)$

Continuous variables –

i.e. variables with continuous range of eigenvalues.

If B has continuous range of eigenvalues: replace sums by integrals:

$$(A_k|) = \int (A_k|B')\,dB'\,(B'|)$$

Normalization: $\sum_n (A_k|B_n)(B_n|A_l) = \delta_{kl}$

or here: $\int (A_k|B')\,dB'\,(B'|A_l) = \delta_{kl}$

But $(B'|A_l) = (A_l|B')^*$

$$\therefore \int (A_k|B')(A_l|B')^*\,dB' = \delta_{kl}$$

if A is energy B momentum $\int (A_k|B')$ [illegible] $\delta(k-l)$

eigenfunction of L_{xy}, appears as f'n of coordinate α.

∴ Orthogonality relation is a special case of its analog, theorem of transformation function. (Found by taking coordinate & mom. themselves).

Now $(A_k|B_m)$ = dimensionless if k, m have discrete values.

But $(A_k|B')$ has dimension $\frac{1}{\sqrt{B}}$ if B f'n continuous eigenvalue.

(Substituting f'n's: dim $\frac{1}{\sqrt{A}}$ or $\frac{1}{\sqrt{B}}$ is ∓ dimension.

Now $\sum_k (B_m|A_k)(A_k|B_n) = \delta_{mn}$

$\sum_k (B'|A_k)(A_k|B'') = ?$ somethg to dimension of B.

can't be δ_{mn} – no meaning; introduce δ-function

if $F(B', B'') = \sum_k (B'|A_k)(A_k|B'')$

appears F in eigen f'n of t;

$$F(B', B'') = \sum \varphi_l \psi_{A_l}(B'')$$

then $\varphi_l = \int \psi^*_{A_l}(B'')\, dB''\, F(B'', B')$

but $\psi^*_{A_l} = (B''|A_l)$

$$\therefore \varphi_l = \int_B \sum_k (B'|A_k)(A_k|B'')\, dB''\, (B''|A_l)$$

$$= \sum_k (B'|A_k)\,\delta_{kl}$$

$$= (B'|A_l).$$

i.e. $F(B', B'')$ is such a f'n that it gives not only the values of B'' different from B';

Hence $F(B', B'') = 0$ if $B'' \neq B'$

[i.e. integral sum f'n F over a range of B'' not including B', get 0

but $\int_{B'-\epsilon}^{B'+\epsilon} F(B', B'')\, dB'' = 1$; (i.e. integral sum f'n over interval incl. B', & get the value of f'n at B'' = B'.

this is called Dirac's δ-function:

$$\delta(B''-B') = 0, \quad B'' \neq B$$

and $\int_{B'-\epsilon}^{B'+\epsilon} \delta(B''-B)\, dB'' = 1$

Oct 31

$$\sum (B'|A_k)(A_k|B'') = F(B', B'') = F_{B'}(B'')$$

We showed that for any ℓ, $\int (B''|A_\ell)(F_{B'}(B'')\, dB'' = (B'|A_\ell)$

also for any ψ: $\int \psi(B'')\, F_{B'}(B'')\, dB'' = \psi(B')$

Whence F must be δ function: $F(B'', B')$ for $B'' = B'$

$\int F\, dB'' = 1$

$\therefore F(B'', B') = \delta(B''-B')$

One considers δ be the limit of a function: (e.g. $\delta(x) = \lim_{\alpha \to 0} e^{-\frac{x^2}{\alpha^2}} \frac{1}{\alpha\sqrt{\pi}}$)

One also defines $\delta(x, y) = 0$ if $x \neq 0$ or $y \neq 0$

and $\int_{-\epsilon}^{\epsilon} \delta\, dx =$

or sometimes, $\delta(\theta, \phi) = 0$ if $\theta \neq 0$ or $\phi \neq 0$

& $\int \delta\, d\Omega = 1$

Suppose A is energy, B is coordinate.

then $(A_k|B'') = \psi_k(B'')$ eigenf'n of kth eigen value of energy.

then $\sum_k \psi_k^*(B')\,\psi_k(B'') = \delta(B''-B')$

If we sum over a finite no. of states:

$$\sum_{k=1}^{N} \psi_k^*(B')\,\psi_k(B'') = \rho(B', B'') \quad \text{— "mixed density"}$$

If we take all states with $\lambda > \lambda_0$, then if B' is more than λ_0 away from B'', ρ is very nearly 0, hence $\rho \simeq \delta(B'-B'')$

In theory of metals — modification of mixed density in calculating correlation energy

In atoms, wave fns "avoid" each other — $\sum \psi_k^*(B')\,\psi_k(B'') \sim 0$ for $B' \neq B''$

In position theory: must sum over all states of neg. energy to find properties; to find physical effect, must subtract actual (infinite) density from that.

look at calculation of correlation energy — Wigner & Seitz P.R. 1933

Suppose A also continuous.

then $\int (B'|A')(A'|B'')\,dA' = \delta(B''-B')$

if B is energy, A the coordinates: continuous eigenf'ns;

they are orthogonal; but $\int (B'|A')\,dA'\,(A'|B') = \int |\psi|^2$ not defined;

but $\int \psi^{E'}\psi^{E''}\,dA' = \delta_{E'-E''}$

$$\therefore \int \psi^{+}_{E'}(x)\,dx \int_{\mathcal{E}} \psi_{E''}(x)\,dE'' = \begin{cases} 0 & \text{if } E' \notin \mathcal{E} \\ 1 & \text{if } E' \in \mathcal{E} \end{cases}$$

We want this to be true:

$$\psi = \sum_n (x|E_n)(E_n|) + \int (x|E')\,dE'\,(E'|)$$

$$(E_n|) = \int (E_n|x)\,dx\,\psi(x)$$

$$(E'|) = \int (E'|x)\,dx\,\psi(x)$$

if this is to be true, must have

In continuum: $(E'|) = \int (E'|x)\,dx \int (x|E'')\,dE''\,(E''|)$ whence we must have

which is ~~$\int \psi^{+}_{E'}\,dx \int \psi_{E''}$~~ $\int (E'|x)\,dx \int (x|E'')\,dE'' = \delta$

If a problem has $V \neq 0$ only in a finite region, ~~then~~ then asymptotically, as $x \to \infty$, E is kinetic: $\frac{p^2}{2m}$. so a momentum state corresponds to an energy state. [e.g. at large distances from atom no V, only kinetic E, & each E has a wave number. Can talk about E, p, or k – all equivalent. ($k = \frac{p}{\hbar}$.

Expand: $\psi = \int (x|E')\,dE'\,(E'|) = \int (x|p')\,dp'\,(p'|)$ or $\int (x|k')\,dk'$

(in eigenf'ns at large distance from force field).

$(x|E')$ differs from $(x|p')$ only by constant factors.

$$(x|E') = \alpha\,(x|p')$$

$$\therefore \int (E'|x)\,dx \int (x|E'')\,dE'' = \begin{cases} 0 \\ 1 \end{cases} \qquad \therefore \alpha^2 \int (p'|x)\,dx \int (x|p'')\,dE'' = \begin{cases} 0 \\ 1 \end{cases}$$

$$\int (p'|x)\,dx \int (x|p'')\,dp'' = \begin{cases} 0 \\ 1 \end{cases} \qquad \therefore \alpha^2 = \frac{dp''}{dE''} \qquad \therefore (x|A') = (x|B')\sqrt{\frac{dB'}{dA'}}$$

Dimensions :

$$[(A_L|B_L)] = 1$$

$$[(A_L|B')] = \frac{1}{\sqrt{B}}$$

$$[(A'|B')] = \frac{1}{\sqrt{AB}}$$

Hence

$$[(x|A')] = \frac{1}{\sqrt{xA}}$$

$$[(x|B')] = \frac{1}{\sqrt{xB}}$$

$$\therefore [(x|A')] = [(x|B')]\left[\sqrt{\frac{B}{A}}\right].$$

Same result.

Nov. #5 [F.D.R. | W.L.W. | U.T. | E.B. | R.S] ELECTION !

$$\int (A'|x')\,dx'\,(x'|A'') = \delta(A''-A')$$

$$\int (A'|x')\,dx' \int_{\mathcal{E}} (x'|A'')\,dA'' = \begin{cases} 1 & A' \in \mathcal{E} \\ 0 & A' \notin \mathcal{E} \end{cases}$$

Hydrogen atom :

$$c_k \frac{\sin(kr-\delta)}{r} Y_{lm}(\theta,\varphi).$$

$$\int |Y|^2\,d\omega = 1$$

$$c_k^2 \int r^2 dr \frac{\sin(kr-\delta)}{r} \int_{k-\epsilon}^{k+\epsilon} \frac{\sin(k'r-\delta)}{r}\,dk'$$

$$= c_k^2 \int_0^\infty \sin(kr-\delta)\,dr \int_{k-\epsilon}^{k+\epsilon} \sin(k'r-\delta)\,dk'$$

$$= c_k \int \sin(kr-\delta)\,dr \left[-\frac{\cos(k'r-\delta)}{r} \Big|_{k-\varepsilon}^{k+\varepsilon} \right]$$

$$= c_k^2 \int \sin(kr-\delta)\,dr \cdot 2\sin(kr-\delta)\,\frac{\sin \varepsilon r}{r}$$

$$= 2c_k^2 \int_0^\infty dr\, \sin^2(kr-\delta)\,\frac{\sin \varepsilon r}{r} = 1$$

in limit as $\varepsilon \to 0$, $k \gg \varepsilon$, and $\sin^2(kr-\delta)$ varies so rapidly in comparison with $\sin \varepsilon r$, that we can replace it by its average $-\frac{1}{2}$.

$$\therefore \quad c_k^2 \int_0^\infty \frac{\sin \varepsilon r}{r}\,dr = 1$$

$$\frac{\pi}{2}\, c_k^2 = 1$$

$$\therefore c_k = \sqrt{\frac{2}{\pi}}$$

Normalization for unit wave number.

Normalization for unit energy: $\sqrt{\frac{2}{\pi}}\sqrt{\frac{dk}{dE}}$ $\qquad \frac{dE}{dk} = \hbar\frac{dE}{dp} = \hbar v$

Matrices representing variable canonically conjugate to diagonal — e.g. how is momentum represented in x-representation?

$$\langle x'|p'|p\rangle = p\,\langle x'|p'\rangle$$

$$= -i\hbar \frac{\partial}{\partial x'}\langle x'|p'\rangle$$

$$\therefore \langle x'|p'\rangle = C\, e^{\frac{i}{\hbar}p'x'}$$

$$= \frac{1}{\sqrt{2\pi}}\, e^{\frac{ip'x'}{\hbar}}$$

momentum "eigenfunction": $\langle p'|E'\rangle = \int \langle p'|x'\rangle\langle x'|E'\rangle = \frac{1}{\sqrt{2\pi}}\int \psi(x)\, e^{-\frac{ip'x'}{\hbar}}\,dx'$

$|(p'|E)|^2$ [illegible] p', [illegible]

[illegible] L —

Wanted: $(x'|p|x'') = \int (x'|p')\,dp'\,p'\,(p'|x'')$

$$= \int \frac{1}{2\pi} e^{\frac{ip'x'}{\hbar}}\, p'\, e^{-\frac{ip'x''}{\hbar}}\, dp'$$

$$= \frac{1}{2\pi} \int p'\, e^{\frac{i}{\hbar}p'(x'-x'')}\, dp'$$

$$= \frac{1}{2\pi}\frac{\hbar}{i}\frac{\partial}{\partial x'} \int e^{\frac{i}{\hbar}p'(x'-x'')}\, dp'$$

$$= -\frac{i\hbar}{2\pi}\frac{\partial}{\partial x'} \int (x'|p')\,dp'\,(p'|x'')$$

$$= -\frac{i\hbar}{2\pi}\frac{\partial}{\partial x'}\,\delta(x'-x'') \qquad !$$

$$= -i\hbar\,\delta'(x'-x'')$$

Matrix [illegible]

derivative of δ - [illegible] !

$\delta(x)$:

$\delta'(x)$:

$\delta'(x) = 0$ for $x \neq 0$.

and $\int_{-\varepsilon}^{\varepsilon} \delta'(x)\,dx = \delta(\varepsilon) - \delta(-\varepsilon) = 0$.

but $\int_{-\varepsilon}^{\varepsilon} x\,\delta'(x)\,dx = 1$

but $\int_{-\varepsilon}^{\varepsilon} x\,\delta'(x)\,dx = \int_{-\varepsilon}^{\varepsilon} \delta'(x)\,x\,dx$

$$= \int_{-\varepsilon}^{\varepsilon} \delta'(x)(\varepsilon - x)\,dx$$

$$= -\int_{-\varepsilon}^{\varepsilon} x\,\delta'(x)\,dx = 1 \qquad !$$

Now $\int f(x)\,\delta(x-x')\,dx = f(x')$.

$$\int f(x)\,\delta'(x-x')\,dx = \delta(x-x')\,f(x)\Big|_{-\infty}^{\infty} - \int \delta(x-x')\,f'(x)\,dx$$

$$= -f'(x').$$

Applying to momentum ~~[illegible]~~ !

$$(x'|p|x'')\,f(x'') = -i\hbar\,\delta'(x'-x'')\,f(x'') \quad = 0 \text{ unless } x = x''$$

$$\int (x'|p|x'')\,dx''\,f(x'') = -i\hbar\,f'(x')$$

Nov. 7

In 3 dimensions, ~~[illegible]~~ need ~~[illegible]~~ 3 coordinates x_1, x_2, x_3; use $x_{1,2,3}$ representation they all commute.

In general, if no symmetry, the ~~[illegible]~~ structure energy levels give a complete description of state.

If there is symmetry – e.g. spherical – state describable by E + M_3. (degeneracy; for different M_3, same E).

Coulomb field: more degeneracy, E, M_3, M^2; (or different quantities in parabolic coordinates).

If E has continuous eigenvalues –

If spherical symmetry, separable in polar coord's –

again E, M^2, M_3 can be quantized.

If E continuous, no sph. symm, E doesn't commute w. M^2, M_3, must have 3 other commuting observables – can use Ξ Θ, Φ direction of motion at large distance from centre of force

---

Some transformations have very simple physical meaning; e.g. transf. from coordinates to momentum simply is – Fourier analysis.

Apply p_x to a function $\psi(x)$.

$$p_x \psi(x) = -i\hbar \frac{\partial}{\partial x} \psi(x)$$

Momentum operator is connected with translations in space.

Angular mom. " " " " " rotation " " "

$$M_z \psi = -i\hbar \frac{\partial}{\partial \varphi} \psi$$

If several particles: $M_{z_1} \psi = -i\hbar \frac{\partial}{\partial \varphi_1} \psi$ – rotation of individual (distinct)

and ~~total orbit~~ $M_z = \sum_k M_{z_k} \psi = -i\hbar \sum_k \frac{\partial \psi}{\partial \varphi_k}$.

M_z corresponds to rotation of whole system (potential energy not changed). (hence $[E, M_z] = 0$)

[In general, an operator associated with a change of a closed system in which potential energy remains unchanged, commutes with energy.]

Total, orbital + spin corresponds to rotation of spin as well as space coord. about z axis.

---

p will commute w. E if translation doesn't change potential (i.e. field-free particle).

Total momentum commutes w. E if only interaction between particles

(i.e. centre of mass moves in field of [illegible])

Finally, $E \to \hbar\omega_c$.

Simply calculate by [illegible] of f.

Sum of states $= \sum_n e^{-\frac{E_n}{kT}}$ (including integral over continuum)

According to maximum sum of diagonal elements,

$\sum_n e^{-\frac{E_n}{kT}}$ is the same for any representation, since it is sum of diagonal elements of $e^{-\frac{H}{kT}}$

$$\therefore \sum_n e^{-\frac{E_n}{kT}} = \mathrm{Spur}\left(x' \middle| e^{-\frac{H}{kT}} \middle| x'\right)$$

$$= \int dx' \left(x' \middle| e^{-\frac{H}{kT}} \middle| x'\right)$$

$$= \int dx' \sum_n (x'|E_n)(E_n| e^{-\frac{H}{kT}} |E_n)(E_n|x')$$

$$= \int dx' \sum_n (x'|E_n)\, e^{-\frac{E_n}{kT}} (E_n|x')$$

$$= \int dx' \sum_n \psi_n^*(x')\, e^{-\frac{E_n}{kT}} \psi_n(x')$$

if we replace kT by $-\frac{i\hbar}{t}$, we have:

$$= \int dx' \sum_n u_n^*(x', s)\, u_n\left(x', -\frac{i\hbar}{kT}\right)$$

where $u_n(x', t) = \psi_n(x')\, e^{-\frac{iE_n t}{\hbar}}$

$$= \int \rho\left(x', s; x', -\frac{i\hbar}{kT}\right) dx'$$

Bloch Function

defines mixed density $\rho(x't'; x''t'') = \sum u_n^*(x't')\, u_n(x''t'')$

Group Theory

In physics only a small part of group theory is used —

Group of cube: those rotations which give the same thing again — i.e. e.g. rotation about 3 axes thru 180°:

E A B C

$A^2 = B^2 = C^2 = E$;

E - identity
A - rotation about x
B - " " y
C - " " z

$EA = A$
$EB = B$
$EC = C$
$AB = C = BA$ (in this case only)
$AC = B = CA$
$BC = A = -B$.

Multiplication table:

	E	A	B	C
E	E	A	B	C
A	A	E	C	B
B	B	C	E	A
C	C	B	A	E

Can have groups with finite or infinite no. of elements

i, -i, -1
(not quite)

Nov. 9 | Any element A times other elements x gives whole group.

The above group is Abelian — i.e. $AB = BA$ etc commutative.

The elements of a group might be represented by a number of things; e.g. transformations in space; permutations, matrices, rotating matrices, etc. —

Simplest group:

	E	A
E	E	A
A	A	E

may represent rotation of line about 180°

or permutation of two ~~elements~~ numbers (1 2);

$E \sim (1\ 1)$

$A \sim (2\ 1)$

or numbers 1, −1;

$E = 1,\ A = -1;$

$(1)(1) = 1$

$(-1)(-1) = 1$

$(-1)(1) = -1$

$(1)(-1) = -1$

These are <u>representations</u> (abstract) of the group: by numbers or matrices obeying same multiplication

With two elements E, A, only one possibility: $A^2 = E$:

With three elements E, A, B:

$A\,E = A$

if $A\,A = E$, must have $A\,B = B$ which is impossible

hence must have $A\,A = B$, $A\,B = E$:

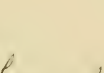
	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

Then $B = A^{-1}$, inverse.

each element of group must have an inverse in the group

i.e. that X for which $AX = E$ is inverse of A.

rotation of equilateral triangle:



$B = A^{-1}$;

also $B = A^{-1}$;

$B^3 = A^3 = E$

or: $\sqrt[3]{1} = \begin{cases} 1 \\ -\frac{1}{2} + \frac{i}{2}\sqrt{3} \\ -\frac{1}{2} - \frac{i}{2}\sqrt{3} \end{cases}$

three possible:

A	B	E
(1)	(1)	(1)
$(-\frac{1}{2} + \frac{i}{2}\sqrt{3})$	$(-\frac{1}{2} - \frac{i}{2}\sqrt{3})$	(1)

one trivial.

Now suppose we have a potential of V such that $V(r)$ is unchanged if $V(r)$ is rotated thru $120°$ around the z-axis. Then $\psi(r)$, $\psi(Ar)$ satisfy the same Schrödinger equation (A represents the rotation). If eigenvalue is non-degenerate,

$$\text{whence} \quad \psi(Ar) = c_A \psi(r).$$

$$\text{also} \quad \psi(Br) = c_A^2 \psi(r)$$

$$\psi(ABr) = \psi(r) = c_A^3 \psi(r)$$

$$\therefore c_A^3 = 1$$

$$\text{and } c_A = \sqrt[3]{1}.$$

$\therefore$ the coefficient c_A is a representation of the group (1.3)

This illustrates one of chief uses of group theory – i.e. to investigate wave-fns under transformations which leave V unchanged; e.g. rotations, in gh. sym. field; or permutations, if many electrons; etc. It turns out that treatment of rotations & permutations can be done without group theory – but it helps give more insight.

Restricted rotation group (finite no of rotations) very useful in theory of vibrations in crystal lattices.

Permutation group in nuclear physics (more different representation than in atomic physics – since two spin states in atoms; 4 in nuclei).

Coming back to the rotation:

Consider a fn $\psi \sim e^{im\phi}$. How does ψ transform under rotation A, B, C:

$$A: \quad \phi \to \phi - 2\pi/3$$

$$\psi \to e^{-im\cdot 2\pi/3}\psi = \left(-\tfrac{1}{2} - \tfrac{i}{2}\sqrt{3}\right)^m \psi .$$

For a single value of m, $m = \text{[illegible]}$, and [illegible] $\sqrt{3}$

for $m = 1, 4, \ldots$ get 1st representation;

" $= 2, 5, \ldots$ " 2nd "

" $= 3, 6, 9 \ldots$ " 3rd " (1, 1, 1)

If we have a fourier-expandable function:

$$\psi \sim \sum_n a_n e^{in\phi}$$

~~these~~ occur in the series: $m = 3n$, n integer; or $= 3n+1$; or $= 3n-1$

Suppose we add to $V(r)$ a small $U(r)\cos 3\phi$;

$$\psi \sim \psi(r)\, Y_{lm}(\theta\phi)$$

$$\sim \psi_r\, P_{lm}(\theta)\, e^{im\phi}$$ E doesn't depend on m

Now consider perturbation $U(r)\cos 3\phi$;

Must consider matrix elements between degenerate states; i.e. splitting levels by perturbation; i.e.: $U(r)\,|\psi(r)|^2\, P_{lm}(\theta)\, P_{l'm'}(\theta)\, e^{i(m-m')\phi} \cos 3\phi \, d\tau$

ϕ integral $\neq 0$ only if $m - m' = \pm 3$.

Hence there are 3 sets of eigenf'ns with same E; and elements only between states of same set.

Hence matrix is: (e.g. for $t=2$)

	2	1	0	-1	-2
$m=$ 2	0	0	0	α	0
1	0	0	0	0	β
0	0	0	0	0	0
-1	α^*	0	0	0	0
-2	0	β^*	0	0	0

And first zero-order approx eigenf'ns

contain either $m = 2, -1$; } zero order
$= 1, -2$; } f'ns;
$= 0$ } but not other mixtures.

Same result as before – i.e. group theory tells us with little work some of properties of eigenf'ns under the perturbation.

Suppose now we have an optical transition polarized in z-direction – must calculate:

$\int \psi_f^* z \psi_i$ $\quad z$ = operator unchanged by A or B.

Hence integral should remain unchanged under rotation

$\therefore \psi_i(A1)\,\psi_f^*(A1) = \psi_i(1)\,\psi_f^*(1)$;

i.e. $c_{Ai}\, c_{Af}^* = 1$

$\therefore c_{Af} = c_{Ai}$ – i.e.

Optical transitions only between states of same representation

---

Nov. 12] Rotations of equilateral triangle.

$E, A, B,$; $B = A^2$, $A = B^2$. $AB = E = A^3 = B^3$.

$\psi(A1) = c_A\, \psi(1) \qquad c_A = \sqrt[3]{1} = \begin{cases} 1 \\ e^{\frac{2}{3}i\pi} \\ e^{-\frac{2}{3}i\pi} \end{cases}$

$\psi(B1) = -B\, \psi(1)$

Consider properties of $\cos m\varphi$, $\sin m\varphi$ under the transformation.

$\Delta \downarrow 1$

$$A: \cos m\varphi \to \cos m(\varphi - \tfrac{2}{3}\pi)$$

$$= \cos\frac{2m\pi}{3}\cos m\varphi + \sin\frac{2m\pi}{3}\sin m\varphi$$

$\psi_1 = \cos m\varphi$

$\psi_2 = \sin m\varphi$

$$A: \sin m\varphi \to \sin m(\varphi - \tfrac{2}{3}\pi)$$

$$\cos\frac{2m\pi}{3}\sin m\varphi - \sin\frac{2m\pi}{3}\cos m\varphi .$$

$$\psi(A1) = a_{11}\psi_1(1) + a_{12}\psi_2(1)$$

$$(c) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \boxed{(b) = \begin{pmatrix} \cos\frac{2m\pi}{3} & -\sin\frac{2m\pi}{3} \\ \sin\frac{2m\pi}{3} & \cos\frac{2m\pi}{3} \end{pmatrix}} \quad (a) = \begin{pmatrix} \cos\frac{2}{3}m\pi & \sin\frac{2}{3}m\pi \\ -\sin\frac{2}{3}m\pi & \cos\frac{2}{3}m\pi \end{pmatrix}$$

If $m = 3n$, $\psi_1(A1) = \psi_1 1$

$m = 3n \pm 1$.

Two-dimensional representation = reps. by matrices of 2 rows & columns.

$$A = \begin{pmatrix} \cos & \sin \\ -\sin & \cos \end{pmatrix}$$

$$B = A^2 = \begin{pmatrix} \cos & \sin \\ -\sin & \cos \end{pmatrix}^2 = \begin{pmatrix} \cos & -\sin \\ \sin & \cos \end{pmatrix}$$

$$AB = \begin{pmatrix} \cos & \sin \\ -\sin & \cos \end{pmatrix}\begin{pmatrix} \cos & -\sin \\ \sin & \cos \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E .$$

If we go from ~~these~~ ψ_i' back to $\psi = e^{im\varphi}$.

$$\psi_i' = \sum_k S_{ik}\psi_k$$

$$\psi_k(A1) = \sum A_{kl}\psi_l(1)$$

$$\psi_i'(A1) = \sum_k\sum_l\sum_m S_{ik}A_{kl}S^{-1}_{lm}\psi_m'(1)$$

$A' = SAS^{-1}$ (matrices transf. of representation)

In this case, though S takes group matrices to diagonal ones simultaneously: $\begin{pmatrix} \lambda & \\ & \lambda \end{pmatrix} = \begin{pmatrix} \lambda & \\ & \lambda \end{pmatrix}$ and get 2 one-dimensional representations. Use say the $\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$ 2-dim. rep. is reducible to 2 one dimensional representations.

In general, an n-dimensional rep. of a group will sometimes be reducible, [to, e.g. 2 $\frac{n}{2}$-dimensional rep.'s] by a unitary transformation [i.e. $S \lambda S^{-1}$ becomes reducible for all λ simultaneously for all λ].

If no such S, representation is irreducible.

Irreducible transf. of certain groups important.

3-dim. rotations:

where $\lambda = 1$ $\begin{matrix} \cos\theta \\ \sin\theta\, e^{i\varphi} \\ \sin\theta\, e^{-i\varphi} \end{matrix}$ or $\begin{matrix} x_1 \\ x_2 \\ x_3 \end{matrix}$

There are infinite linear combinations, each other by rotations; some of them are always transformed into themselves.

But if we have six f'ns: $\cos^2\theta$, $\sin^2\theta\, e^{2i\varphi}$, $\sin^2\theta\, e^{-2i\varphi}$, $\sin\theta\cos\theta\, e^{i\varphi}$, $\sin\theta\cos\theta\, e^{-i\varphi}$, $\sin^2\theta$

which is commutative under rotation. Hence G abelian. Group can be broken up into one 5 one 1 [illegible] representation

---

Group of 4 elements.

Two distinct ones.

	E	A	B	C
E	E	A	B	C
A	A	E	C	B
B	B	C	E	A
C	C	B	A	E

or

	E	A	B	C
E	E	A	B	C
A	A	E	C	D
B	B	C	A	E
C	C	D	E	A

$\longrightarrow$

$A^2 = E$
$B^2 = A$
$B^3 = AB = C$
$B^4 = A^2 = E$
$C^2 = B^6 = A$
$C^3 = B^9 = C$
$C^4 = B^{12} = E$

$A^2 = E$
$A^3 = A$
$A^4 = E$

I

$A^2 = E$
$B^2 = E$
$C^2 = E$

$AB = C$
$BC = A$
$CA = B$.

elements the same.

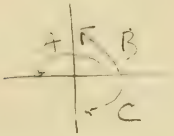
rotations of [illegible]
(e.g. circle)

II B & C the same.

3 kinds of elements:
E, A, B & C.

Group rotations of square in plane.

II - by giving representation of B (or C) we get rest of them.



$BC = E$
$B^2 = C^2 = A$
etc.

$B^2 = E$ ia $\quad C_B^2 = 1$

$\therefore C_B = 1, i, -1, -i$.

$C_A = -C_B^2 = 1, -1, 1, -1$

$C_C = 1, -i, -1, i$

$C_E = 1, 1, 1, 1$.

$C^{i\,m\,4}$, $m = 4m$, $4m+1$, $4m+2$, $4m+3$

4 representations.

in case I : $c_A^2 = 1$ $c_B^2 = 1$ $c_C^2 = 1$

$c_A = \pm 1$ $c_B = \pm 1$ $c_C = \pm 1$

4 representations :

E	1	1	1	1
A	1	1	-1	-1
B	1	-1	1	-1
C	1	-1	-1	1

Nov. ~~15~~ 14.

Group all ? whose elements can be got from taking powers ? one ? the elements is a cyclic group. ; and every such group can be represented by roots ? unity.

If we have a cyclical group $O(h)$, $A^h = E$;

then $c_A = \sqrt[h]{1} = e^{\frac{2\pi i}{h} k}$

$k = 0, 1 \cdots h$

True representation : each element represented by a different unity or number

Untrue " : several " " " the same " " " .

for $k = 1$ always get a True rep.

for $k = 0$, " " an untrue rep; namely, unit

Four group : $A^2 = B^2 = C^2 = E$;

$AB = C$
$BC = A$
$CA = B$

we have 4 untrue rep. ? the group.

For a true rep.; if you know one, you know all the rest.

Five elements ; only the cyclic group . (as always for primes).

Wigner - VII - IX

Six elements :

	E	A	B	C	D	E
E	E	A	B	C	D	E
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
E	E	B	C	A	E	D

Not Abelian.

group of permutations of three ~~permutation~~

permute 123 : 213 132 321 312 231

E A B C D E

$A^2 = B^2 = C^2 = E$; but $D^2 = F$, $F^2 = D$

$AB = D$ $AC = F$ $BC = D$
$BA = F$ $CA = D$ $CB = F$

$DF = FD = E$.

It has subgroups ; (EA (EB) (EC) (EDF) are all groups by themselves .

E A
A E

E B
B E

E C
C E

E D F
D F E
F E D

Co-sets : take elements of sub-group & multiply by an element not in the subgroup . If subgroup E contains g elements, each coset contains g elements ;

e.g : a coset of (AE) is B, AB
EB = (BD) in this case .

~~the~~ another is EC : (C, AC), = (C, F) .

n^{th} coset given by $E X_n$ if X_n is any element of nth coset.

cosets not groups .

Subgroups $\underline{G}_1 \quad \underline{G}_2 \quad \underline{G}_3 \quad \ldots$

$\underline{G}_n X_m = \underline{G}_n$ cosets $\qquad \underline{G}\, \underline{G}_m = g\, \underline{G}_n$

$\underline{G}\, X_n X_m = \underline{G}_n\, \underline{G}_m$

Two cosets identical or no elements are identical in all elements.

The cosets form a group, with the original subgroup the unit element + cosets the other elements. $gx = h$

Hence order of subgroups n = no. of cosets including subgroup

and hence divisor of order of group g = order of subgroup

if h is prime: no non-trivial subgroups. h = order of original group

In this case $h = 0$, no other subgroups until $g = 2, 3$.

Classes. take any group elements X, A + form $X^{-1}AX$;

for an Abelian group $X^{-1}AX = A$.

not identical!

e.g. in above group,

$C^{-1}AC = CF = B$

$B^{-1}AB = BD = C$

$D^{-1}AD = FB = C$

$F^{-1}AF = DC = B$

$A^{-1}AA = \qquad = A$

$E^{-1}AE = \qquad\qquad A$

all elements, other than $X^{-1}AX$, all elements of group, form a class.

$A^{-1}DA = A \quad = A$

Here E, A, B, C, D, F, form classes.

any element belongs to one & only one class.

If order of group is prime, it is cyclic, hence Abelian, and each element forms its own class.

In above group, E : no permutation.

A, B, C : ~~two~~ one permutation interchanges

$D\ F$: two ~~rotation~~ interchanges.

Cubic group: x, y, z can be interchanged.

hence 6 permutations.

sign of any coord can be interchanged!

8 possibilities;

$\therefore\ 6 \cdot 8 = 48$ elements !.

Classes : $C_1 = E$ 1

C_2 : rotations about one of cubic axes thru $180°$ 3

C_3 : " " " " " " $90°$ 6

C_4 : " " body diagonal thru $120°$ 8

C_5 " " face " " $180°$ 6

24

these 24 form subgroup of pure rotation.

For each of these classes there is another class, for which one takes mirror images:

I : inversion

IC_2 : " mirror at cubic planes

IC_3 — — —

etc.

Nov. 10

E belongs to every subgroup:

E " " one & only one class (namely, class consisting of E a

I a good, we don't belong to any subgroup, but stands alone.

Multiplication of classes:

Consider classes C_i & C_k.

$$X_i^{-1} A_i X_i = A_i' \qquad X_k^{-1} A_k X_i = A_k'$$

multiply $C_i C_k$:

in general, $C_i C_k$ contains elements of other classes; if it contains one, it contains all; If a product can be obtained in more than one way, all other products can be obtained in the same no. of ways. i.e. product contains all elements of class the same no. of times.

e.g. in 6-group:

$(C_3)^2 = C_3 + 2C_1$

$(C_1)^2 = C_1$

$(C_2 C_3) = 2C_2$

$(C_2)^2 = 3C_1 + 3C_3$

$C_1 C_2 = C_2$

$C_1 C_3 = C_3$

Mult. table of classes in ↗:

C_1	C_2	C_3
C_2	$3(C_1+C_3)$	$2C_2$
C_3	$2C_2$	C_3+2C_1

Representation: reducible if a many. can simultaneously transform all matrices of group to $\left(\begin{array}{c|c} & 0 \\ \hline 0 & \end{array}\right)$ form.

If none such can be found, irreducible representation.

Operations corresponding to transformation of some of x's.

$\psi_i(Rx) = \sum_l A_{il}\, \psi_l(x)$, A_{il} is matrix representation of group.

Any representation can be transformed to a unitary one.

$S^{-1} A_k S$ = unitary matrix

Consider $\sum_k A_k A_k^\dagger = H$. $\dagger$ = ~ *

then H is Hermitian [for $H_{il} = \sum_k \sum_j A_{ij} A_{lj}^\dagger$

$= \sum_k \sum_j A_{ij} A_{lj}^*$

$H_{li} = \sum_k \sum_j A_{lj} A_{ji}^\dagger$

$= \sum_k \sum_j A_{lj} A_{ij}^*$

$= H_{il}^*$

$\mathcal{U}^{-1} H \mathcal{U} = d$ – diagonal matrix.

Then $d^{-1/2} \mathcal{U}^{-1} H \mathcal{U} d^{1/2} = 1$

Can show that $d^{-1/2} \mathcal{U}^{-1} A_k \mathcal{U} d^{1/2}$ are unitary, for all k

See Wigner, pp 81-82.

If $A_k M = M A_k$ for all k, $M_{ik} \neq i_k S_{ik}$,

then the representation is reducible.

(& only then) If $A_k M = M A_k$

then $M^\dagger A_k^\dagger = A_k^\dagger M^\dagger$

and $A_k M^\dagger A_k^\dagger A_k = A_k A_k^\dagger M^\dagger A_k$

$\therefore A_k M^\dagger = M^\dagger A_k$ (if A_k are unitary) so they can be, [illegible] diagonalized

A_k also commute w. $M + M^\dagger$ & $i(M - M^\dagger)$.

$M + iM^\dagger$ are Hermitian

& $i(M - M^\dagger)$ [illegible]

Hence the sets - Hermitian matrices which commute with all proj elements.

Then — find — S such that:

$$S^{-1} M S \text{ : diagonal;}$$

then $S^{-1} A_\kappa S \cdot S^{-1} M S = S^{-1} M S \cdot S^{-1} A_\kappa S$.

But $S^{-1} A_\kappa S = \bar{A}_\kappa$ is a new matrix representation.

and $S^{-1} M S = d$, diagonal;

and $\bar{A}_\kappa d = d \bar{A}_\kappa$.

Now suppose $d_{ii} \neq d_{kk}$;

then $\bar{A}^\kappa_{ik} d_{kk} = d_{ii} \bar{A}^\kappa_{ik}$;

$\therefore \bar{A}_{ik} = 0$;

Thus if we order d like this: $\left(\begin{array}{c|c|c|c} d_1 & & & \\ \hline & d_2 & & \\ \hline & & d_3 & \\ \hline & & & \ddots \end{array}\right)$

and A_κ = 0 outside of diagonal squares:

where A is indivisible. $\left(\begin{array}{c|c|c|c} \cdot & \cdot & \cdot & \cdot \\ \hline \cdot & \cdot & \cdot & \cdot \\ \hline \cdot & \cdot & \cdot & \cdot \\ \hline \cdot & \cdot & \cdot & \cdot \end{array}\right)$

(if d contains different elements).

[if d ~~set~~ is not unitary, $M = S^{-1} d S^{-1}$, use a diagonal unitary matrix to transform)

Nov 19

1. Group representation are unitary.

2. If M commutes with all the group matrices, the group representation is reducible, or else M is a multiple of 1.

3. Schur's Lemma.

If we have 2 representations $D^{(1)}(A_x)$, $D^{(2)}(A_x)$.

dim. l_1 l_2

suppose a matrix M s.t.:

(M has l_1 colums, l_2 rows.)

$$M D^{(1)}(A_x) = D^{(2)}(A_x) M \quad \text{for all } x.$$

Then either $M \equiv 0$, $\leftarrow l_1 \neq l_2$

or $|M| = 0 \leftarrow l_1 = l_2$

If $|M| \neq 0$, then M^{-1} can be found;

then $D^{(1)} = M^{-1} D^{(2)} M$, and

$D^{(1)}$ + $D^{(2)}$ are equivalent.

i.e.: If $D^{(1)}$ + $D^{(2)}$ are non-equivalent irreducible representations, then $M = 0$

$$M D^{(1)} = D^{(2)} M.$$

$$\therefore D^{(1)\dagger} M^{\dagger} = M^{\dagger} D^{(2)\dagger}$$

If group matrices are unitary, $D^{(1)\dagger}(A_x) = D^{(1)}(A_x^{-1}) = D^{(1)}[A_x^{-1}]$

$D^{(2)\dagger} = D^{(2)-1}(A_x) = D^{(2)}[A_x^{-1}]$.

$$\therefore D^{(1)}[A_x^{-1}] M^{\dagger} = M^{\dagger} D^{(2)}[A_x^{-1}].$$

$$\therefore D^{(1)}[A_x] M^{\dagger} = M^{\dagger} D^{(2)}[A_x]$$

then $M D^{(1)} M^{\dagger} = M M^{\dagger} D^{(2)}$

$$M D^{(1)} M^T = M M^T D^{(2)}$$

but $M D^{(1)} = D^{(2)} M$;

$$\therefore \quad D^{(2)} M M^T = M M^T D^{(2)}$$

$\therefore$ $(M M^T)$ commutes with D^2;

but since $D^{(2)}$ is irreducible, by previous theorem,

$$M M^T = c\, I$$

Case $l_1 = l_2$: If $c \neq 0$, then $\| M M^T \| = c^{l_1} \neq 0$.

$$\| M \| \| M^T \| \neq 0.$$

~~therefore~~ $\| M \| \neq 0$, and $D^1 + D^2$ ~~equivalent~~

If $c = 0$, $\quad M M^T = 0$,

$$\sum_i M_{ki} M_{ik}^T = \sum_i M_{ki} M_{ki}^*$$

$$= \sum_i |M_{ki}|^2 = 0$$

$\therefore$ $M_{ki} = 0$ (all positive)

$\therefore$ $M = 0$.

($l_2 - l_1$ zeros).

Case $l_1 \neq l_2$:

amplify M: $\begin{pmatrix} M_{11} \cdots M_{1l_1} & 0 \cdots 0 \\ \vdots & \\ M_{l_2 l_1} & 0 \cdots 0 \end{pmatrix} = N$

$$(M M^T)_{ij} = \sum_k M_{ik} M_{kj}^T$$

$$= \sum_{k=1}^{l_1} M_{ik} M_{jk}^*$$

$(N N^T)_{ij} = (M M^T)_{ij}$ (other term vanishes)

Then [illegible] $= 0$

$\therefore\ M \equiv 0$ as before.

If we construct an M which has the property, we have, $\forall$ [illegible] to get

$$M = \sum_R D^{(2)}(R)\, X\, D^{(1)}(R^{-1}).$$

X is an arbitrary matrix of same dim. as M.

$$D^{(2)}(S)\, M = \sum_R D^{(2)}(S)\, D^{(2)}(R)\, X\, D^{(1)}(R^{-1})$$

$$= \sum D^{(2)}(SR)\, X\, D^{(1)}(R^{-1}).$$

if $R' = SR$, $R = S^{-1}R'$, $R^{-1} = R'^{-1}S$; as R goes thru all group elements so does R'.

$$\therefore\ D^{(2)}(S)\, M = \sum_{R'} D^{(2)}(R')\, X\, D^{(1)}(R'^{-1}S)$$

$$= \sum D^{(2)}(R')\, X\, D^{(1)}(R'^{-1})\, D^{(1)}(S)$$

$$= M\, D^{(1)}(S).$$

Hence we must have:

(if $D^{(1)}, D^{(2)}$ inequivalent, + both irreducible)

$$\sum_R D^{(2)}(R)\, X\, D^{(1)}(R^{-1}) = 0.$$

Take $X_{lm} = 1$, $X_{l'm'} = 0$ if $l' \neq l$ and $m' \neq m$

$$\therefore\ M_{in} = \sum_R \sum_{k,n} D^{(2)}(R)_{ik}\, \delta_{kl}\, \delta_{mn}\, D^{(1)}(R^{-1})_{nj}$$

$$= \sum D^{(2)}(R)_{il}\, D^{(1)}(R^{-1})_{mj} = 0 \quad \text{for any } i, l, m, j$$

If D is unitary: $D_{mn}(R^{-1}) = D^{*}_{nm}(R)$

then $\sum_R D^{(1)}_{ik}(R)\, D^{(2)*}_{nm}(R) = 0$.

If $D^{(1)} = D^{(2)}$: $M = \sum_R D^{(1)}(R)\, X\, D^{(1)}(R^{-1})$

and $M D^{(1)}(S) = D^{(1)}(S) M$; from

theorem two, $M = c\, 1$ (c depends on X).

$$M_{in} = \sum_R D^{(1)}_{ik}(R)\, D^{(1)*}_{nm}(R) = c\, \delta_{im}$$

$$\sum_n M_{nn} = \sum_n \sum_R D_{nk}\, D_{mn}(R^{-1})$$

$$= \sum_R \sum_n D_{mn}^{-1}\, D_{nk}$$

$$= \sum_R D_{mk}(R^{-1}R) = \sum_R \delta_{mk} = h\, \delta_{mk}$$

$$\Omega = \sum_n c_{km} = c_{km}\, l_1$$

$$\therefore c_{km}\, l_1 = h\, \delta_{mk}$$

$$\therefore c_{km} = \delta_{km} \frac{h}{l_1} .$$

$$\therefore \sum_R D^{j}_{ik}(R)\, D^{j'*}_{nm}(R) = \delta_{jj'}\, \delta_{in}\, \delta_{km} \frac{h}{l_j}$$

Nov 26 1940

Theorem concerning group representations:

$$\sum_R D^{(j)}_{\mu\nu}(R)\, D^{(j')}_{\rho\sigma}(R) = \delta_{jj'}\, \delta_{\mu\rho}\, \delta_{\nu\sigma}\, \frac{h}{l_j}.$$

h = no of elements in group.
l_j = dimension of j representation.

$$\sum_P c_j(P)\, c_{j'}^*(P) = \delta_{jj'}\, h.$$

Application of group theory is to problems having ill well defined symmetry. eg: If $\psi(\underline{r})$ belongs to E, with V spherically symmetrical, then for any rotation P, $\psi(P\underline{r}) = \psi(\underline{r})$.

If operation P leaves Hamiltonian invariant, and $\psi(\underline{r})$ is sol'n of Schrödinger eq'n for energy E, then $\psi(P\underline{r})$ is a sol'n belonging to same energy. For: $H(\underline{r})\psi(\underline{r}) = E\,\psi(\underline{r})$.

or $H(P\underline{r})\,\psi(P\underline{r}) = E\,\psi(P\underline{r})$

but $H(P\underline{r}) = H(\underline{r})$

$\therefore \quad H(\underline{r})\,\psi(P\underline{r}) = E\,\psi(P\underline{r})$.

If degenerate, orthonormal sol'ns $\psi_\mu(\underline{r})$ for E:
$\mu = 1, \ldots, l$:

Then $\psi_\mu(P\underline{r})$ is a sol'n corr. to E;
since ψ_μ - one complete set:

$$\psi_\mu(P\underline{r}) = \sum_\nu D_{\mu\nu}(P)\,\psi_\nu(\underline{r}).$$

D's give representation of symmetry group — i.e. of operators which leave Hamiltonian unchanged. They form a group since if $H(P\underline{r}) = H(\underline{r})$, $H(Q\underline{r}) = H(\underline{r})$, then $H(QP\underline{r})$

e.g., group of rotations, for spl. symm. hamiltonian;

permutation group, for atom. of system with several electrons

$$\left[H = \sum_{i=1} \frac{p_i^2}{2m} + \sum \frac{e_i^2}{r_i} + \sum_{i,k} \frac{e_i^2}{r_{ik}} \right].$$

Sys. in electric field: group of rotations about axis of field.

+ mirror image resp to plane containing field direction

" " magnetic " : group of rotations about axis but not mirror image in

+ mirror image w. resp. to plane ⊥ to field direction.

" " crystalline field : symmetry of crystal.

$D_{\mu\nu}(P)$ gives representation of group;

for: $\psi(PQ) = \sum_\nu D_{\mu\nu}(P)\psi_\nu(Q)$

$$= \sum_\rho D_{\mu\rho}(P)\psi_\rho(Q) = \sum_{\rho\nu} D_{\mu\rho}(P) D_{\rho\nu}(Q)\psi_\nu(\ )$$

$$\therefore D(PQ) = D(P)\,D(Q).$$

since there are l ψ_ν's, D is an l-dimensional representation of the group, the general P. in.

If rep. is irreducible, need all l ψ's;

If rep. is reducible, ψ's fall into several sets, such that ψ's of each set only transform among themselves under symmetry operations.

Accidental degeneracy: If ψ's belonging to given E correspond to a reducible representation

e.g.: levels of alkali atom: ~~no degeneracy~~ only l specified, n ...

$(2l+1)$ ψ's, $m = -l, -l+1, \ldots, 0, \ldots, l-1, l$.

Transformation of ψ's under rot. corr. to irreducible repr. of rotation group of dimension $2l+1$ (only one such repr.).

But H contains: n, n^2 ψ's in ordinary case $l = 0, 1, \ldots, n$

levels of same n different + accidentally degenerate.

due to potential $\therefore$

$\therefore$ H contains a feature which is purely accidental which one the atom in a free hydrogen atom — alkali is better —

(1) Regarding accidental degeneracy, transformation of ψ's by group E corr. to irreducible representation of group.

$$\psi_\mu(P r) \qquad \psi_\rho(P r) = \sum_\sigma D_{\rho\sigma}(P)\, \psi_\sigma(r)$$

$$\sum_P \psi_\mu(P r)\, \psi_\rho^*(P r) = \sum_{\nu\sigma} D_{\mu\nu}(P)\, D^*_{\rho\sigma}(P)\, \psi_\nu \psi_\sigma^*$$

$$= \delta_{\mu\rho} \sum_{\nu\sigma} \delta_{\nu\sigma}\, \psi_\nu \psi_\sigma^* \frac{h}{g}$$

$$= \frac{h}{g}\, \delta_{\mu\rho} \sum_\nu |\psi_\nu|^2$$

Relation: $\int \psi_m(P r)\, \psi_n^*(P r)\, dP = 0$

Relation: $\sum_{P\,\mu} \psi_\mu \psi_\mu^* = 0$

But: $\frac{1}{h} \sum_P |\psi_\mu|^2(P r) = \text{average over all } P = \frac{1}{g} \sum_\nu |\psi_\nu|^2(r) = \text{average over all } \psi$

Nov. 28 | $\frac{1}{n}\sum_p |\psi_n(P\,\mathbf{r})|^2 = \frac{1}{n}\sum_p |\psi_n(\mathbf{r})|^2$!!

Suppose V is spherically symmetric —
Then group of transl. is group of all rotations in space

$\therefore \sum_m |\psi_{lm}(\mathbf{r})|^2$ is invariant against rotation (since both sides also inv.)

i.e. subshell charge density is spherically symmetric.
(I have gases sph. symm.)

for $\nu = 0$, only one term on right. $\therefore$ $|\psi_1|^2$ is sph. symm. for ground state.

Consider atom in cubically symmetrical field; for Na in Na cryst.
then average charge distrib. must have cubic symmetry.

Axial field: axially symmetrical $\sum_n |\psi_n|^2$

Inversion: $\mathbf{r} \to -\mathbf{r}$ average charge density invariant against inversion

If Ham. is invariant under both inversion & rotation —

$$RI = IR;$$

E	I	R
I	E	R'
R	R'	E

$\therefore$ E, I are a subgroup
E, R " " "

If we have representation $D(R)$, $C(E, I)$

$$D(R)C(I) = D'(RI).$$

C: $E = 1$, $I = \begin{Bmatrix} 1 \\ -1 \end{Bmatrix}$ $\quad D'(R) = D(R)$, $\quad D'(E, I) = C(E, I)$.

$$D'(RI) = \pm D(R).$$

inversion cutting sign of eigenfns, a lemma to alone.

Parity - even & odd.

Rotation group: 1 irreducible representation of any dimension.

1 one dimensional : each element = 1.

1 2 - " : $\pm\frac{1}{2}$ spinor transformation.

1 3 - " : $\cos\theta$ $\sin\theta e^{i\phi}$ $\sin\theta e^{-i\phi}$ or $x\,y\,z$;
$J=1$
gives transformation of coordinates —
or vectors " " any vector.

1 4 - " : $x^2 - y^2$ -

1 5 - " : $J=2$ Tensor transformation.

Wigner

$2J+1^{th}$ " repr : J

Value of J completely determines behavior of wave function of system under rotation

---

Permutations .. many representations —

Pauli theorem says that sum over all ~~permutations~~ $\sum_{p^n} \psi_{p^n}$ must be invariant against permutation of electrons ; hence it is symmetrical in all electrons.

(Pauli principle says this for whole f'n (space × spin) — but the spin in that space f'n also is symmetrical —)

Spin f'ns : 2 el., $\alpha(1)\,\alpha(2)$, $\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)$, $\beta(1)\,\beta(2)$ } $S=1$ transform like vectors under rotation, invariant under permutation.

$\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)$ - $S=0$ - invariant under rotation antisymm under permutation

Space f'n must have opposite symmetry as spin f'n so that the product is antisymm - for Pauli principle.

Very complicated for [illegible] el.

With an external field, only axial symmetry, hence no. of group elements is reduced –

Consider matrices of element of orthogonal group in the representation of the original (sph.-sym.) group – It may be possible to find a ~~[illegible]~~ transformation reducing these.

e.g. if field is along z-axis: thence only changes of azimuth φ permitted – Matrices of elements corresponding to rotation about z can be reduced to

$$\begin{vmatrix} |\phi_{m}| & \\ & \end{vmatrix}$$

– + energy levels in effect no field –

Nov. 30

H_0 original Hamiltonian
H perturbed " ;

suppose the symmetry functions of H are a subgroup of sym. g. of H_0

Call P_0 the sym. functions of H_0
P " " " " H.

Representations $D(P_0)$, $D(P)$.

$\underline{P}$ state of energy $\underline{E}$.

Perhaps $D(P)$ is reducible:

$$S^{-1} D S = D'(P)$$

Where $D'_{jk}(P) \neq 0$ only if j & k belong to same subset of quasi-[illegible]

$$D' : \begin{vmatrix} \square & 0 & 0 & \cdot \\ 0 & \square & 0 & 0 \\ 0 & 0 & \square & 0 \\ \cdot & 0 & 0 & \cdot \end{vmatrix}$$

then in field H only the eigenf'n's belonging to little diagonal square are degenerate

i.e. level E_0 is split up into several different energies, corresponding to sets of degenerate ψ's of H^0; by the perturbation
↳ irreducible representations of group of H –

example:

In homogeneous el. field;

rotations about field axis

reflections of plane thru field

reflection: $e^{im\phi} \to e^{-im\phi}$

$e^{im\phi}$, $e^{-im\phi}$ belong to same representation of group

Rotation about ϕ_0: $R = \begin{pmatrix} e^{im\phi} & 0 \\ 0 & e^{-im\phi} \end{pmatrix}$.

Reflection: $D = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$.

$m = 0$, 1 dimensional representation.

$m \neq 0$, 2 " " .

If H_0 is invariant against rotation about origin:

$$P_l^m(\theta)\, e^{im\phi}.$$

$$D \begin{array}{c} m=0 \\ m=-1 \\ m=1 \\ \vdots \end{array} \begin{pmatrix} \times & & & & & & & \\ & \times & \times & \times & & & & \\ & \times & \times & \times & & & & \\ & & & & \times & \times & \times & \\ & & & & \times & \times & & \\ & & & & \times & & \times & \\ & & & & & & \times & \times \\ & & & & & & & \text{etc.} \end{pmatrix}$$

(reduced into irreducible representations of group of perturbation H)

e.g. if $l = 3$, splits into 4 levels, each corr. to $|m| = 0, 1, 2, 3$.

Group theory gives these results for any magnitude of perturbation –

Electric field: perturbation F_z;

matrix elements of perturbation. $\int \psi_n^* F_z \psi_m = 0$ if ψ_m & ψ_n have same parity.

∴ el. field has vanishing matrix elements between degenerate states;

to get the splitting, have to take 2nd order approximation

hence one wonders whether further approx. makes further change; but group theory tells me a priori what splitting there is.

Magnetic field:

Symmetry properties:

Rotation about field.

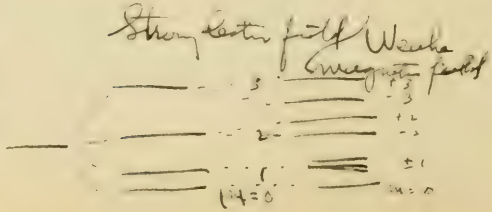
Reflection at plane ⊥ to field: $\varphi \to \pi - \varphi$.

$\hookrightarrow P_l^m(\theta) \to (-1)^{l+m} P_l^m(\theta)$.

all matrix elements of perturbation equal, get $2l+1$ new eigenvalues for each value of m

Level: $D(P)$: $\begin{pmatrix} \times & & \\ & \times & \\ & & \times \\ & & & \ddots \end{pmatrix}$ one eigenvalue for each value of m

~~Strong~~

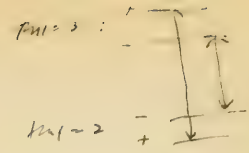


$\Delta E = H \mu g m$.

This separation [illegible] in magnetic

Invasion of the level in walls of earth:

much bigger slope than normal —



It is important to know what irreducible representations are contained in the reducible part of a representation — (as above). For instance, let there be a unitary function like $D^{j}_{\mu\nu}$ above,

$$\sum_{P} D^{j}_{\mu\nu}(P)\, D^{j'*}_{\rho\sigma}(P) = \delta_{jj'}\,\delta_{\mu\rho}\,\delta_{\nu\sigma}\,\frac{h}{k_j}.$$

Consider an h-dimensional space; where we employ the group elements $P_1, P_2, \ldots$ hence fixed a pt. corresponding to $D^{j}_{\mu\nu}(1)$ (coordinates of pt. = values of $D^{j}_{\mu\nu}$ for each P) then $D^{j}_{\mu\nu}(1)$ is — h-dimensional vector; one vector for each (j, μ, ν). and across theorem simply say: these vectors are orthogonal.

For a given j, (k_j^2) vectors (k_j values of μ & ν).

$\therefore$ as we sum over j get $\sum_j k_j^2 \leq h$, since we can't have more than h orthogonal vectors — $\therefore$ no. of irreducible representations is finite, for a finite group.

Class C: $\quad X^{-1} C_i^{(k)} X = C_j^{(k)} \quad$ X any element of group —

p classes. then $D(X^{-1})\, D(C_i^{(k)})\, D(X) = D(C_j^{(k)})$.

We know that spur D remains invariant under similarity transformations; spur $D = \sum_\mu D_{\mu\mu}(C^h)$.

$\therefore$ spur remains the same for all elements of class

Call spur the character of representation $\chi(C)$.

character is the same for all elements of a class.

$\therefore$ can use characters instead of elements to specify gp

(e.g. cubic group, 48 elements, 10 classes).

Mon 3 Dec. Character $\chi(C) = \sum_h D^j_{hh}(P)$. is the same for all elements of a class.

Orthogonality: $\sum_P D^j_{\mu\nu}(P)\, D^{j'*}_{\mu'\nu'}(P) = \delta_{jj'}\delta_{\mu\mu'}\delta_{\nu\nu'}\frac{h}{f_j}$.

Now $\sum_P \chi_j(P)\,\chi_{j'}^*(P) = \sum_P \sum_h \sum_l D^j_{hh}(P)\, D^{j'*}_{ll}(P) = \delta_{jj'}\frac{h}{f_j}$

$= \delta_{jj'}\, h$.

if n_k is no of group elements in class C_k.

$$\sum_k \frac{n_k}{h}\,\chi_j(C_k)\,\chi_{j'}^*(C_k) = \delta_{jj'}$$

$\therefore \sqrt{\frac{n_k}{h}}\,\chi_j(C_k)$ is a vector in class-space;

p-dimensional - p classes

there can not exist more than p orthogonal vectors

$\therefore$ no. of representations $\leq$ no. of classes — !

Before we had $\sum_j l_j^2 = h$.

We multiplied classes: $C_k C_l = \sum_m a_{klm} C_m$ + put the classes in a form of times -

Conversely the quantity $\sum_{P \subset C_k} D^j(P)$; it must commute with all matrices of the group; for $X^{-1} C_k^\nu X = C_k^\nu$

$$\therefore C_k^\nu X = X C_k^\nu \quad \text{if } \nu \text{ covers all elements of class, we have } \mu\text{ s}$$

$$\therefore X \sum_{P \subset C_k} D^j(P) = \sum_{P \subset C_k} D^j(P) X$$

$$\therefore \sum_{P \subset C_k} D^j(P) = c\,1 \quad \text{a multiple of unit matrix.}$$

Now $\sum_m \sum_{P \subset C_k} D^j_{mm}(P) = n_k \chi_j(C_k)$

but also $\sum_m \sum_{P \subset C_k} D^j_{mm}(P) = c \sum_m 1 = c\, l_j$

$$\therefore c\, l_j = n_k \chi_j(C_k).$$

$$\therefore c = \frac{n_k \chi_j(C_k)}{l_j}$$

Now $D^j(P) D^j(Q) = D^j(PQ)$.

$$\sum_{P \subset C_k} \sum_{Q \subset C_l} D^j(P) D^j(Q) = \sum_{P,Q} D^j(PQ) = \sum_m a_{klm} \sum_{R \subset C_m} D^j(R)$$

$$\downarrow$$

$$\frac{n_k n_l \chi_j(C_k) \chi_j(C_l)}{l_j^2} = \sum a_{klm} \frac{n_m \chi_j(C_m)}{l_j}$$

but $\chi_j(E) = l_j$: $\quad \therefore n_k n_l \chi_j(C_k) \chi_j(C_l) = \sum_m a_{klm}\, n_m \chi_j(C_m)\, \chi_j(E)$

Reducible representation $= \sum b_j D^j$ (i.e. rep. D^j occurs b_j times in the reducible representation)

then $\chi(C_k) = \sum_j b_j \chi_j(C_k)$

and $\sum_k n_k \chi_{j'}^*(C_k)\chi(C_k) = \sum_k \sum_j b_j n_k \chi_{j'}^*(C_k)\chi_j(C_k)$

$$= \sum_j \delta_{jj'} b_j h = b_{j'} h .$$

$$\therefore b_j = \frac{1}{h} \sum_k n_k \chi_{j'}^*(C_k)\chi(C_k) .$$

Regular Representation

suppose $PQ = R$.

suppose h rows & columns ; $Q \cdot\cdot \begin{pmatrix} \cdot & 0 & \overset{R}{\vdots} & 0 \end{pmatrix}$

$E = I$;

$P \neq E$ has no diagonal elements .

show that there is a representation :

give here the elements P, P' :

$$(PP')_{QR} = \sum_S P_{QS} P'_{SR} = \sum_S \delta_{S,PQ}\, \delta_{R,P'S} = \delta_{R,P'PQ} = 1 \text{ if } R = P'PQ$$

Reg. Rep: $\chi(E) = h$, or

$\chi(C_k) = 0$ for $C_k \neq E$.

$\therefore$ reg. rep. contains [illegible] $b_j = \chi^*_j(E) = l_j$ of times

$\therefore$ Reg. Rep. $D_r = \sum l_j D^j$

Dec 5. We were proving: $\sum_j l_j^2 = h$

No. of irreducible reps. = p. no. of classes.

Had found that regular rep. contains each irreducible representation l_j times: $D_r = \sum l_j D^j$.

Got that from expansion theorem: no. of times j irred. rep. occurs, b_j is given by: $b_j = \frac{1}{h} \sum_k n_k \chi_j(C_k) \chi^*(C_k)$ (given character)

Regular rep: $\chi(E) = h$

$\chi(P) = 0$, $P \neq E$.

whence $b_j = \chi_j(E) = l_j$.

Now $\sum_P |\chi(P)|^2 = \sum_{P, j, j'} b_j \chi_j(P) b_{j'} \chi_{j'}^*(P)$.

$= \sum_{jj'} b_j b_{j'} \sum_P \chi_j(P) \chi_{j'}^*(P)$

$= \sum_j |b_j|^2 h$

Smallest possible value of $\sum |\chi(P)|^2$ is h.

If this is so, the rep. is irreducible, for then one $b_j = 1$, others 0.

For a regular rep.: $b_j = l_j$, and $h \sum |l_j|^2 = \sum_P |\chi(P)|^2 = h^2$

Now $\sum_j \chi_j(C_h)\, l_j = 0$ unless $C_h = E$?

$$\sum_j \chi_j(E)\, \chi_j(C_h) = n\, \delta_{h,1} \quad \text{if } C_h = E.$$

since $l_j = \chi_j(E)$ for regular repr.

We had:

$$n_h n_l\, \chi_j(C_h)\, \chi_j(C_l) = l_j \sum_m a_{hlm}\, n_m\, \chi_j(C_m)$$

sum over j:

$$n_h n_l \sum_j \chi_j(C_h)\, \chi_j(C_l) = \sum_m a_{hlm}\, n_m \sum_j \chi_j\, \chi_j(C_m)$$

$$= \sum_m a_{hlm}\, n_m\, \delta_{m,1}$$

$$= a_{hl1}\, n_1 \qquad n_1 = 1.$$

Take an element X_h of class C_h.

X_h^{-1} belongs to a class C_{-h}, say.

and all X_h^{-1} belong to same class C_{-h}.

since all inverses of elements of C_{-h} belong to C_h.

Now $C_h C_{-h}$ gives E n_h times + other ones:

$$C_h C_{-h} = n_h E + \cdots$$

$$\therefore a_{hl1} = \begin{cases} n_h & \text{if } l = -h \\ 0 & \text{otherwise.} \end{cases}$$

Now $D(X)_l \; D(X_l^{-1}) = 1$

D is unitary; $\therefore D^{-1} = D^{*}$

$D^{-1}_{ij} = D^{*}_{ij}$

$\therefore \chi(X_h^{-1}) = \chi^{*}(X_h)$

if a class is its own inverse, it must have a real character; otherwise, it is the complex conjugate $\therefore$

$$\therefore \; n_h \sum_j \chi_j^{*}(C_l)\, \chi_j(C_h) = \delta_{hl}\, h.$$

(since $n_l n_l \sum \chi_j(C_h)\chi_j(C_l) = a_{hl}, h = \delta_{hl}\, n_h\, h$

$$\therefore \; n_l \sum \chi_j(C_h)\, \chi_j(C_l) = \delta_{hl}\, h.$$

new orth. rel: or $n_l \sum_j \chi_j^{*}(C_h)\, \chi_j(C_l) = \delta_{hl}\, h$.

Orth. rel. no 1: χ_j is a vector in class-space of p-dimensions

$\therefore$ the no. g of irreducible reps. is $g \le p$.

Orth. rel. no 2: $\chi_j(C_l)$ is vector in representation-space of g-dimensions

$\therefore$ the no p of classes is $p \le g$;

$\therefore p = g$.

i.e. no. of irreducible reps. of group = no. of classes.

Example: cubic group: 48 elements, 10 classes.

Pure rotations: 24 " 5 "

Inversions: 24 " 5 "

$\therefore$ 5 representations / permutation group —

$\sum n_j^2 = 24$

$\therefore$ $2 \cdot 3^2 + 1 \cdot 2^2 \cdot 2 \cdot 1^2$

$\therefore$ 2 3-dim. irr. non-equivalent
1 2-dim. "
2 1-dim. " " " "

Consider group E, I : 2 irrep : $\begin{array}{cc} E & I \\ 1 & 1 \\ 1 & -1 \end{array}$

& get whole group from

this + rotation group.

	E	C_2	C_3	C_4	C_5
	identity	rot. thru π about two axis	rot. thru $2\pi/3$ about three axis	rot. thru π about four axis	rot. thru $2\pi/5$ about five axis
	1	3	6	6	8

Each class is its own inverse

$\therefore$ real characters.

Find characters / classes. From Ch. Pl. g. 2 (1+0

get 5 representations $\Gamma_{1,2,3,4,5}$.

Γ_1	1	1	1	1	1
Γ_2	1	1	-1	-1	1
Γ_3	2	2	0	0	-1
Γ_4	3	-1	1	-1	0
Γ_5	3	-1	-1	1	0

Dec. 7.

~~E C2 C3 C4 C5~~

$$P_\ell^m(\theta)\, e^{im\phi}$$

rotate thru ϕ_0: multiply by $e^{im\phi_0}$.

then $\chi(\phi_0) = \sum_{m=-\ell}^{\ell} e^{im\phi_0} = \dfrac{\sin(\ell+\frac{1}{2})\phi_0}{\sin \phi_0/2}$.

cubic group is subgroup of rotation group; can get it by rotation about particular axes; above expression is not for any axis. We had rotations:

	E	C_2	C_3	C_4	C_5
$\phi_0 =$	0	π	$\frac{2\pi}{3}$	π	$\frac{2\pi}{5}$
$\chi(\phi_0)$:	$2\ell+1$	$(-1)^\ell$	$+1$ $\ell = 3n$ -1 $\ell = 3n+1$ $+1$ $\ell = 3n+2$	$(-1)^\ell$	$+1$, $\ell = 5n$ 0 $\ell = 5n+1$ -1 $\ell = 5n+2$

$$\therefore\ \chi_\ell(C_k) = \sum b_{\ell j}\, \chi_j(C_k)$$

rotation group. irreducible cubic character

	$\chi_j(E)$	$\chi_j(C_2)$	$\chi_j(C_3)$	$\chi_j(C_4)$	$\chi_j(C_5)$	
$\ell = 0$	1	1	1	1	1	$\longrightarrow \Gamma(1)$
1	3	-1	1	-1	0	$\longrightarrow \Gamma(4)$
2	5	1	-1	1	-1	$\longrightarrow \Gamma(3) + \Gamma(5)$
3	7	-1	-1	-1	1	$\longrightarrow \Gamma_2 + \Gamma_4 + \Gamma_5$
4	9	1	1	1	0	$\longrightarrow \Gamma_1 + \Gamma_3 + \Gamma_5 + \Gamma_5$
5	11	-1	1	-1	-1	$\longrightarrow$
6	13	1	-1	1	1	

etc.

$\therefore\ \delta(\alpha j) = 0, 1,$ no splitting of s, p. levels in cubic field

$j = 2\ 3\ 4$ ~~[illegible]~~ 2 3 4 levels; $j = 5\ 6$, 4, 6 levels.

Rare-earth salts show this splitting —

incomplete 4-f shells.

4-f shell is low in atom, not much disturbed when atom is put in crystal. It gives rise to rather complicated magnetic moments; get much complicated by large j due to interaction of electrons; if it were about zero, would be used up in small bonds; (e.g. $\frac{1}{2}-\frac{1}{2}$ 0, $\frac{3}{2}-\frac{3}{2}$ 0) ~~to~~ shorter forces along to put open multi-parallel

But when large avg. mom. is due to interaction of electrons, it isn't interacted w. neighboring atoms. 4f electrons are subject to a field of crystal; if it is cubic, get splitting as predicted. (but analysis is difficult, because of lack of knowledge of states intermediate coupling — several 4f states — figure out cases!)

Van-Vleck — magnetic effects — usually in agreement.

Multiplication of ~~Representations~~ . .

Imagine two ~~electrons~~: $Y_{l_1 m_1}(\theta_1, \varphi_1)$ $Y_{l_2 m_2}(\theta_2, \varphi_2)$.

Describe atom by product of such Y's.

rotation leaves ~~interaction~~ interaction unchanged

∴ want to have representation which leaves product of Y's unchanged

Suppose we have representations D_1, D_2 for electrons;

Represent by $D_1 \times D_2$, representation of product $j_1 \times j_2$ — each unit of product $\times$ is obtained by multiplying an element of D_1 by one of D_2. $j_1 \cdot j_2$ rows + columns.

$$\text{or} \quad \chi = \sum_{i,j} \chi^{(1)}_{ij} D^{(2)}_{ij} = \chi^{(1)} \chi^{(2)}$$

but $\chi^{(1)} \chi^{(2)} = \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} e^{i m_1 \phi_1 + i m_2 \phi_2}$ $\quad m = m_1 + m_2$

$$= \sum_{L=|l_1-l_2|}^{l_1+l_2} \sum_{m=-L}^{L} e^{im\phi}.$$

$\therefore$ the reducible representation generated by product splits up into irreducible representations: each split into terms of $|l_1-l_2| \ldots l_1+l_2$

$$= \sum_{L=|l_1-l_2|}^{l_1+l_2} \chi_L .$$

Optical transition probabilities —

$$\int z \, \psi_{i\mu} \psi^*_{f\nu} \, d\tau$$

i.e. rotate all these factors simultaneously —

z transforms according to $D^{(1)}$

$\psi_{i\mu}$ " " " $D^{(l)}$

$\psi_{f\nu}$ " " " $D^{(l')}$.

then $D^{(1)} \times D^{(l)} \times D^{(l')} = D^0 + \text{others}$

This can be only if $D^{(1)} \times D^{(l)}$ contains $D^{(l')}$.

this only if $\underline{l' = l \pm 1, l}$ — trivial

for ~~other~~ rotating prop. but not for cubic.

Do something about —

Dec. 15. 1940.

Dirac Relativistic Equation: R.R.S. 1927.

The relativistic Schroedinger eq'n (also Klein Gordon) –

Use: $E = V + \frac{p^2}{2m}$ for ordinary mech:

then: $i\hbar \frac{\partial}{\partial t}\psi = \left\{V + \left(-\frac{\hbar^2}{m}\right)\Delta\right\}\psi$.

E: $i\hbar \frac{\partial}{\partial t}$

p_x: $-i\hbar \frac{\partial}{\partial x}$

etc.

so that group vel. particle vel:

$e^{\frac{i}{\hbar}(p\cdot r - Et)}$

Relativistic mechanics:

$(W-V)^2 = c^2p^2 + m^2c^4$ m rest mass

$W = E + mc^2$.

then: $\left(i\hbar\frac{\partial}{\partial t} - V\right)^2\psi + c^2\hbar^2\Delta\psi - m^2c^4\psi = 0$

For electromagnetic field: $p \to p - \frac{e}{c}A$.

then:

K. G. $\left\{\left(i\hbar\frac{\partial}{\partial t} - V\right)^2 - c^2\left(-i\hbar\,\mathrm{grad} - \frac{e}{c}\underline{A}\right)^2 - m^2c^4\right\}\psi = 0$

Contains 2nd derivative of time.

then $\frac{\partial^2\psi}{\partial t^2} = O\psi + P\frac{\partial\psi}{\partial t}$.

∴ must give not only ψ but also $\dot{\psi}$ to get $\ddot{\psi}$

whereas ordinary wave mech., gives only ψ, & get $\dot{\psi}$ –

This has as consequence that energy is no longer positive definite

for a known wave f'n gives $\pm(W-V)$ for energy –

$W - V = \pm\sqrt{c^2p^2 + m^2c^4}$.

This was bad — in fact charge densities weren't + definite either. [Cf. post., here $\psi^* \frac{\partial \psi}{\partial t} - \psi \frac{\partial \psi^*}{\partial t} = \rho$, $\underline{j} = \psi^* \text{grad}\, \psi - \psi\, \text{grad}\, \psi^*$

$\rho, \underline{j}$ form a 4-vector

ρ may be + or − . This, Dirac said, ~~contradicts~~ experience — (no positrons known then) — also, spin wasn't very well taken care of — hence he looked for another equation — which would give a definite sign for charge density, like non-rel. Schr. theory. in which $\rho = \psi^*\psi$ (hence any theory which gives ρ as $\Sigma \psi^* \psi$ will be OK — but not if it has derivatives.

∴ Dirac postulates ~~that~~ (ρ should be this sort) ; only possible if eq'n. has only 1st time derivative occurs. But in relativ. theory, time + space coords enter in same way — hence only 1st order space derivatives as well.

Now in C. M. theory, we have a wave eq'n :

$$\nabla^2 E - \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2} = 0$$

K. G. eq'n with $V = 0$: $\nabla^2 \psi - \frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} = \left(\frac{mc}{\hbar}\right)^2 \psi$.

But in E+M. case, we have Maxwell eq'ns :

(field free space)

$\frac{1}{c} \dot{H} = -\nabla \times E$ 1st order eqns — hence just like non Dirac equation —

$\frac{1}{c} \dot{E} = \nabla \times H$

But each Maxwell eq'n contains different quantities (Ξ, r), 3 components in each case). $\frac{\partial \Xi}{\partial t}$

$$w = \frac{1}{8\pi}(E^2 + H^2) = \frac{1}{8\pi}\sum_{k=1}^{6} \psi_k^2 - \phi$$

this form we want for charge density -

I introduce wave f'n of several components ψ_k

In general, we might have :

$$\frac{1}{c}\frac{\partial \psi_k}{\partial t} = \sum_\lambda a^x_{k\lambda}\frac{\partial \psi_\lambda}{\partial x} + a^y_{k\lambda}\frac{\partial \psi_\lambda}{\partial y} + a^z_{k\lambda}\frac{\partial \psi_\lambda}{\partial z}$$

Connecting components of ψ $\qquad + \frac{mc}{\hbar}\cdot b_{k\lambda}\psi_\lambda$;

or : $$\frac{1}{c}\frac{\partial \psi_k}{\partial t} = \left(a^x\frac{\partial \psi}{\partial x} + a^y\frac{\partial \psi}{\partial y} + a^z\frac{\partial \psi}{\partial z}\right)_k + \frac{mc}{\hbar}(b\psi)_k$$

(a-v first i in bottom)

$$= (\underline{a}\cdot \text{grad}\,\psi)_k + \frac{imc}{\hbar}(b\psi)_k .$$

or : $$\frac{1}{c}\frac{\partial \psi}{\partial t} = \underline{\alpha}\cdot \text{grad}\,\psi + i\frac{mc}{\hbar}\beta\psi .$$

This must give K-G. eq'n when squared -

$$\frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} = \left(\underline{\alpha}\cdot\underline{\text{grad}} + i\beta\frac{mc}{\hbar}\right)^2\psi$$

$$= \Big[\alpha_x^2\frac{\partial^2}{\partial x^2} + \alpha_y^2\frac{\partial^2}{\partial y^2} + \alpha_z^2\frac{\partial^2}{\partial z^2} - \beta^2\frac{m^2c^2}{\hbar^2}$$

$$+ (\alpha_x\alpha_y + \alpha_y\alpha_x)\frac{\partial^2}{\partial x\partial y} + \cdots \Big]\psi .$$

$$+ \alpha_x\beta + \beta\alpha_x\frac{\partial}{\partial x} + \cdots$$

this is K. G. - eq'n if we

have : $\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1$,

$$\alpha_x\alpha_y + \alpha_y\alpha_x = 0$$
$$\alpha_x\alpha_z + \alpha_z\alpha_x = 0$$
$$\alpha_y\alpha_z + \alpha_z\alpha_y = 0$$
$$\alpha_x\beta + \beta\alpha_x = 0$$

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if $\begin{cases} \alpha_i \alpha_k + \alpha_k \alpha_i = 2\delta_{ik} \\ \alpha_i \beta + \beta \alpha_i = 0 \end{cases}$ $\beta^2 = 1$.

then $\frac{1}{c}\frac{\partial \psi}{\partial t} = \left(-\underline{\alpha} \cdot \text{grad} + \frac{imc}{\hbar}\beta\right)\psi$ → analogous to Maxwell eq'ns

gives $\frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} = \left(\nabla^2 - \frac{m^2c^2}{\hbar^2}\right)\psi$ → analogous to wave eq'n

How many rows & columns for α's & β's?

look at $\alpha_i \alpha_k + \alpha_k \alpha_i = 2\delta_{ik}$: there we had below, for the spin matrices: $\underline{\sigma} = \begin{pmatrix} \hbar & i-i \\ i+i & -\hbar \end{pmatrix}$.

e.g.: $\sigma_x \sigma_y = i\sigma_z$ ∴ $\sigma_x \sigma_y + \sigma_y \sigma_x = 0$.
$\sigma_y \sigma_x = -i\sigma_z$ etc.

also $\sigma_i^2 = 1$;

∴ spin matrices would work, if we had only 1st condition;
but not have a β which anticommutes with all these;

There is no 4th 2 row matrix which commutes with all of these -
(for these three with don't matrix form a complete set) -
try iterating σ's; ∴ 4 row matrices:

σ_x: $\alpha_x : \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix}$ $\alpha_y : \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix}$ | σ_z: $\begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix}$

these still anticommute -

$\alpha_x \alpha_y = \begin{pmatrix} \sigma_x \sigma_y & 0 \\ 0 & \sigma_x \sigma_y \end{pmatrix}$ etc.

another which anticommutes with all of α's is $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$\alpha_x \alpha_y + \alpha_y \alpha_x = \begin{pmatrix} \sigma_x \sigma_y + \sigma_y \sigma_x & 0 \\ 0 & \sigma_x \sigma_y + \sigma_y \sigma_x \end{pmatrix}$

$\alpha_x \beta = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & -\sigma_x \\ \sigma_x & 0 \end{pmatrix}$ ∴ anticom

$\beta \sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} = \begin{pmatrix} 0 & \sigma_x \\ -\sigma_x & 0 \end{pmatrix}$

$= 0$

Therefore ψ has 4 components — $\begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\end{pmatrix}$ $(\psi_1^*\ \psi_2^*\ \psi_3^*\ \psi_4^*)$

$$\alpha_1 = \begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix} \quad \alpha_2 = \begin{pmatrix}0&0&0&-i\\0&0&i&0\\0&-i&0&0\\i&0&0&0\end{pmatrix}$$

$$\alpha_3 = \begin{pmatrix}0&0&1&0\\0&0&0&-1\\1&0&0&0\\0&-1&0&0\end{pmatrix} \quad \beta = \begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}$$

$$\frac{1}{c}\frac{\partial\psi_1}{\partial t} = -\frac{\partial\psi_4}{\partial x} + i\frac{\partial\psi_4}{\partial y} - \frac{\partial\psi_3}{\partial z} + \frac{imc}{\hbar}\psi_1$$

$$\frac{1}{c}\frac{\partial\psi_2}{\partial t} = -\frac{\partial\psi_3}{\partial x} - i\frac{\partial\psi_3}{\partial y} + \frac{\partial\psi_4}{\partial z} + \frac{imc}{\hbar}\psi_2$$

$$\frac{1}{c}\frac{\partial\psi_3}{\partial t} = -\frac{\partial\psi_2}{\partial x} + i\frac{\partial\psi_2}{\partial y} - \frac{\partial\psi_1}{\partial z} - \frac{imc}{\hbar}\psi_3$$

$$\frac{1}{c}\frac{\partial\psi_4}{\partial t} = -\frac{\partial\psi_1}{\partial x} - i\frac{\partial\psi_1}{\partial y} + \frac{\partial\psi_2}{\partial z} - \frac{imc}{\hbar}\psi_4$$

or, if $\psi_j \sim e^{-\frac{iE}{\hbar}t}$

$$-\frac{i}{\hbar c}\left[E+mc^2\right]\psi_1 = \frac{\partial\psi_4}{\partial x} - i\frac{\partial\psi_4}{\partial y} + \frac{\partial\psi_3}{\partial z}$$

$$\text{"} \quad \psi_2 = \frac{\partial\psi_3}{\partial x} - i\frac{\partial\psi_3}{\partial y} - \frac{\partial\psi_4}{\partial z}$$

$$-\frac{i}{\hbar c}\left[E-mc^2\right]\psi_3 = \frac{\partial\psi_2}{\partial x} - i\frac{\partial\psi_2}{\partial y} + \frac{\partial\psi_1}{\partial z}$$

$$\text{"} \quad \psi_4 = \frac{\partial\psi_1}{\partial x} + i\frac{\partial\psi_1}{\partial y} - \frac{\partial\psi_2}{\partial z}$$

Non-rel. limit, $E - mc^2 \sim -mc^2$. $\psi_1, \psi_2 \ll \psi_3\ \psi_4$.

In non-relativistic approx, get Schrödinger eq'n, in presence of electric field, get Pauli eq'n's.

I. investigate relativistic invariance —
Read Pauli's article, Handbuch 24/1.

Relativistic invariance means that the form

) the equations remain the same when we make,

a linearly independent or rotation (if the various

components transform into each other)

i.e. if ψ moves with respect to S with velocity v, then we

must have: $\frac{1}{c}\frac{\partial \psi'}{\partial t'} = \alpha \cdot \text{grad}' \psi' + \frac{i m c}{\hbar} \psi'$

where ψ' is transform of ψ.

I maintain is proven if we can write down $\psi'_\lambda = \sum_\lambda a_{\kappa\lambda} \psi_\lambda$

satisfies this - an infinitesimal linear transformation.

(in this case, get $a_{\kappa\lambda} = \delta_{\kappa\lambda} + \varepsilon \alpha^\nu \beta_{\kappa\lambda}$ etc.

Dec. 17. Dirac: $\frac{1}{c}\dot{\psi} + \underline{\alpha}\cdot\text{grad}\,\psi - \frac{imc}{\hbar}\beta\psi = 0$ $\quad \psi^* \rightarrow$ multiply

$\frac{1}{c}\dot{\psi}^* + \underline{\alpha}^*\cdot\text{grad}\,\psi^* + \frac{imc}{\hbar}\beta^*\psi^* = 0$ $\quad \leftarrow \psi$ & add.

$$\frac{1}{c}(\psi^*\dot{\psi} + \dot{\psi}^*\psi) + \psi^*\underline{\alpha}\cdot\text{grad}\,\psi + \underline{\alpha}^*\cdot\text{grad}\,\psi^*\psi - \frac{imc}{\hbar}(\psi^*\beta\psi - \beta^*\psi^*\psi)$$

Now $\psi^*\alpha_x\frac{\partial\psi}{\partial x} = \sum_\lambda \psi^*_\lambda\alpha_\lambda\frac{\partial\psi}{\partial x} = \sum_{\kappa\lambda}\psi^*_\kappa\alpha_{\kappa\lambda}\frac{\partial\psi_\lambda}{\partial x}$.

$$\alpha^*_x\frac{\partial\psi^*}{\partial x}\cdot\psi = \sum_{\kappa\lambda}\alpha^{*x}_{\kappa\lambda}\frac{\partial\psi^*_\kappa}{\partial x}\cdot\psi_\lambda = \frac{\partial\psi^*}{\partial x}\tilde{\alpha}^*\psi$$

$$\therefore\ (\underline{\alpha}^*\cdot\text{grad}\,\psi^*)\psi = (\text{grad}\,\psi^*\cdot\tilde{\underline{\alpha}}^*)\psi$$

and $\beta^*\psi^* = \psi^*\tilde{\beta}^*$.

$$\therefore\ \frac{1}{c}(\psi^*\dot{\psi} + \dot{\psi}^*\psi) + \psi^*\underline{\alpha}\cdot\text{grad}\,\psi + \text{grad}\,\psi^*\cdot\tilde{\underline{\alpha}}^*\psi - \frac{imc}{\hbar}(\psi^*\beta\psi - \psi^*\tilde{\beta}^*\psi)$$

To get continuity eq^n, must have term with derivation vanish, i.e. $\beta = \tilde{\beta}^*$. omitted

~~$\frac{\partial(\psi^*\psi)}{\partial t}$~~

If further, $\alpha = \tilde{\alpha}^*$,

we have:

$$\frac{1}{c}\frac{\partial(\psi^*\psi)}{\partial t} + \text{div}\,\psi^*\underline{\alpha}\psi = 0.$$

$\therefore\ \psi^*\psi = \rho$: charge density

$\therefore\ c\psi^*\underline{\alpha}\psi = \underline{j}$: current density.

Now $\dot{A} = \frac{i}{\hbar}(HA - AH)$.

In Dirac theory: $H = -i\hbar c\,\underline{\alpha}\cdot\text{grad} - mc^2\beta$
$= c\underline{\alpha}\cdot\underline{p} - mc^2\beta$

if $A = q$: $HA - AH = c\underline{\alpha}\cdot\underline{p}\,q - mc^2\beta q - qc\underline{\alpha}\cdot\underline{p} + mc^2 q\beta$

$$HA - AH = -\sum_q \alpha_q p_q - \alpha_q q p_q = -i\hbar c\,\alpha_q$$

$$\therefore \quad \dot{q} = \frac{i}{\hbar}[HA - AH]$$

$$= \frac{i}{\hbar} \cdot -i\hbar c\,\alpha_q = c\,\alpha_q$$

$$\therefore \quad \dot{q}_{mn} = c\,\alpha_{q\,mn} = c\int \psi_m^* \alpha_q \psi_n \, d\tau = \frac{i}{\hbar}(E_m - E_n)\psi_{mn}$$

External fields :— $E^2 = c^2p^2 + m^2c^4$

$$(E - V)^2 = c^2\left(\underline{p} + \tfrac{e}{c}\underline{A}\right)^2 + m^2c^4$$

and $H = V + c\,\alpha\cdot\left(\underline{p} + \frac{e}{c}\underline{A}\right) - mc^2\beta$

$$= V + \alpha\cdot(c\underline{p} + e\underline{A}) - mc^2\beta$$

$$\therefore \quad \frac{1}{c}\frac{\partial\psi}{\partial t} = -\frac{i}{\hbar c}V\psi - \alpha\cdot\text{grad}\,\psi - \frac{ie}{\hbar c}\alpha\cdot\underline{A}\psi - \frac{imc}{\hbar}\beta\psi.$$

Nothing is changed in previous derivation of continuity equation

(if V, A are real) still have $\rho = \psi^*\psi$

$\underline{j} = \psi^*\underline{\alpha}\psi$

Likewise, still have $\dot{q} = c\,\alpha_q$.

Now $\dot{p}_q = \frac{i}{\hbar}(Hp_q - p_qH)$

$$= \frac{i}{\hbar}\left(H\frac{\partial}{\partial q} - \frac{\partial}{\partial q}H\right) \cdot -i\hbar$$

$$= -\frac{\partial}{\partial q}(V + e\,\alpha\cdot\underline{A})$$ as in classical mech.

~~$\dot{m}\dot{q} = p_q + \frac{e}{c}A_x$~~

Field free : $e^{-iEt/\hbar}$:

$$\psi^* \partial_x \mid E\psi = c\,\underline{\alpha}\cdot\underline{p}\,\psi - mc^2\beta\,\psi$$

$$E\psi^* = \underline{p}\,\psi^*\cdot\alpha - \psi^* mc^2\beta \mid \alpha_x\psi$$

$$2E\,\psi^*\alpha_x\psi = c\left[\psi^*\alpha_x\underline{\alpha}\cdot\underline{p}\,\psi + \underline{p}\,\psi^*\cdot\alpha\,\alpha_x\psi\right] - mc^2\psi^*(\alpha_x\beta\psi - \beta\alpha_x\psi)$$

$$= c\left[\psi^* p_x\psi + p_x^*\psi^*\psi + \psi^*\alpha_x\alpha_y p_y\psi - p_y^*\psi^*\alpha_y\alpha_x\psi\right]$$

$$p_y = -i\hbar\frac{\partial}{\partial y}$$

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$$\therefore\ \frac{\partial E}{\partial}\psi^*\alpha_x\psi = -i\hbar\left[\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi + \psi^*\alpha_x\alpha_y\frac{\partial\psi}{\partial y} + \frac{\partial\psi^*}{\partial y}\alpha_x\alpha_y\psi\right]$$

$$= -i\hbar\left[\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right] + \hbar\frac{\partial}{\partial y}(\psi^*\sigma_z\psi) - \hbar\frac{\partial}{\partial y}\psi^*\sigma_z\psi$$

$\alpha_x\alpha_y = i\sigma_z$

$$\therefore\ \psi^*\underline{\alpha}\cdot\psi = -\frac{i\hbar c}{2E}\left(\psi^*\,\mathrm{grad}\,\psi - \psi\,\mathrm{grad}\,\psi^*\right) + \frac{\hbar c}{2E}\nabla\times(\psi^*\underline{\sigma}\psi)$$

σ is constant with complete [illegible].

Integrate over all space; if ψ vanishes at infinite [illegible]

$$\int\psi^*\underline{\alpha}\,\psi = -\frac{i\hbar c}{E}\int\psi^*\,\mathrm{grad}\,\psi$$

$$= \frac{c}{E}\int\psi^* p\,\psi$$

i.e. $\left(\frac{\underline{v}}{c}\right) = \frac{c}{E}(p)$ (classical relativistic diagnostic [illegible])

$\underline{\sigma}$-[illegible]: [illegible]

Angular Momentum

Classically: $M_3 = x p_y - y p_x$.

$$\dot{M}_3 = \frac{i}{\hbar}(HM_3 - M_3 H) \qquad H = c\,\underline{\alpha}\cdot\underline{p} - mc^2\beta$$

$$= \frac{i}{\hbar}(\underline{\alpha}\cdot\underline{p}\,M_3 - M_3\,\underline{\alpha}\cdot\underline{p}) - \frac{i}{\hbar}(\alpha_x p_x x p_y - x p_y \alpha_x p_x + y p_y \alpha_y p_x - y p_x \alpha_y p_y)$$

$$= \frac{i}{\hbar}(x\alpha_x p_y(i\hbar) + x\alpha_y p_x(-i\hbar)) = -(x\alpha_x p_y - y\alpha_y p_x).$$

or $\quad \dot{\underline{M}} = c\,\underline{\alpha}\times\underline{p}$.

$\underline{S} = \frac{1}{2}\hbar\,\underline{\sigma}$ $\qquad$ Now $\alpha_x\alpha_x\alpha_y = -\alpha_x\alpha_y\alpha_x$

$\underline{S}_3 = -\frac{1}{2}\hbar\,\alpha_x\alpha_y$ $\qquad$ $\alpha_y\alpha_x\alpha_y = -\alpha_x\alpha_y\alpha_y$

$\dot{\underline{S}}_3 = \frac{1}{2}[H, \alpha_x\alpha_y]$ $\qquad$ $\alpha_3\alpha_x\alpha_y = \alpha_x\alpha_y\alpha_3$

$\beta\alpha_x\alpha_y = \alpha_x\alpha_y\beta$

$$\dot{S}_3 = \frac{1}{2}c\left[\underline{\alpha}\cdot\underline{p}, \alpha_x\alpha_y\right] = \frac{c}{2}\left[p_x\cdot 2\alpha_y + p_y(-2\alpha_x)\right]$$

$$= -(p_x\alpha_y - \alpha_x p_y) = -\dot{M}$$

$$\therefore \quad \dot{M} + \dot{S} = 0, \text{ or } \frac{d}{dt}(M+S) = 0$$

$$M + S = \underline{x}\times\underline{p} + \frac{1}{2}\hbar\,\underline{\sigma}.$$

Conservation of $(M+S)$, [illegible] $\underline{M}$ [illegible] $\underline{S}$ [illegible] $\underline{M}$, usually $\underline{M}$, [illegible] $\underline{S}$ [illegible]

σ_3 is diagonal, has eigenvalues ± 1. $\begin{pmatrix} 1 & & & \\ & -1 & & \\ & & 1 & \\ & & & -1 \end{pmatrix}$

if ψ has only ψ_1, ψ_3, then $\sigma_3\psi_{1,3} = \psi_{1,3}$ and S_3 has value $\hbar/2$. if it has only $\psi_{2,4}$, $\sigma_3\psi_{2,4} = -\psi_{2,4}$ and S_3 has value $-\hbar/2$.

spin comes naturally from Dirac equation — one of the great successes of Dirac theory.

Hamiltonian: [illegible] spin-orbit.

$\therefore$ [illegible]

$\therefore$ [illegible] relativistic correction.

$\therefore$ [illegible] the spin comes as part of total angular momentum.

In field, Dirac equation: $i\hbar\frac{\partial}{\partial t} = V + i\hbar c\,\underline{\alpha}\cdot\text{grad} - e\,\underline{\alpha}\cdot\underline{A} + mc^2$

Consider: $\left(i\hbar\frac{\partial}{\partial t} - V + i\hbar c\,\underline{\alpha}\cdot\text{grad} + e\underline{\alpha}\cdot\underline{A} + mc^2\beta\right)\psi = 0$

$-\left(i\hbar\frac{\partial}{\partial t} - V\right)^2\psi + \left(i\hbar c\,\text{grad} - eA\right)^2\psi + (mc^2)^2\psi + \text{other terms}.$

terms mixing α_x, β vanish; [illegible]

~~[illegible]~~ also mixed derivatives vanish; and mixed potential [illegible]

V, grad don't commute. get terms like $\alpha_x\alpha_y\left(\frac{\partial A_x}{\partial x} - \frac{\partial A_y}{\partial x}\right)$.

$\leftarrow$ E $\qquad$ $\uparrow$ H

Jan 6 1941 $\quad$ if $V = V(r)$, $\underline{A} = 0$, $\quad$ [illegible] $+ \frac{1}{2}\hbar\underline{\sigma}$ is constant of motion

$\frac{d\underline{p}}{dt} = 0$

$\frac{d\underline{p}}{dt} = -\frac{\partial}{\partial\underline{r}}(V + c\,\underline{\alpha}\cdot\underline{p})$

$L\psi = \underline{\alpha}\cdot\underline{p} + \beta mc^2 + V - V\psi$

[illegible]

[illegible] $L\psi^* + \psi = -\frac{i\hbar c}{2}\psi^*(\text{grad} + eA)(V - \psi)$ [illegible]

Dirac equation

$$\left(\frac{i}{c}\frac{\partial}{\partial t} + \underline{\sigma}\cdot\left(\underline{p} + \frac{e}{c}\underline{A}\right) + \frac{e}{c}\underline{\sigma}\cdot\underline{H} - \frac{e}{c}V\right)\psi = 0$$

Operate on the left $\left(-\frac{i}{c}\frac{\partial}{\partial t} + \underline{\sigma}\cdot\left(\underline{p} + \frac{e}{c}\underline{A}\right) + \frac{e}{c}\underline{H} + \frac{e}{c}V\right)$

then gives: $\left[-\left(\frac{i}{c}\frac{\partial}{\partial t} - \frac{e}{c}V\right)^2 + \left(\underline{p} + \frac{e}{c}\underline{A}\right)^2 - \frac{m^2c^2}{\hbar^2} - \frac{e}{c}\underline{\sigma}\cdot\underline{H}\right]\psi = 0$

normal Dirac with the addition $-\frac{ie}{\hbar c}\frac{\partial A}{\partial t} + \frac{e}{c}(\underline{A}\cdot\underline{p} + \underline{p}\cdot\underline{A})$

$$\left[-\frac{e}{\hbar c}\underline{\sigma}\cdot\left(\frac{i}{c}\frac{\partial\underline{A}}{\partial t} + \frac{\partial\phi}{\partial\underline{r}}\right)\right]$$

$$= \frac{ie}{\hbar c}\underline{\alpha}\cdot\underline{E}$$

$$\left(\left(\frac{i}{c}\frac{\partial}{\partial t} - V\right)^2 - c^2\left(\underline{\sigma}\cdot\left(\underline{p} - \frac{e}{c}\underline{A}\right)\right)^2 - m^2c^2 - \frac{ie}{\hbar}\underline{\alpha}\cdot\underline{E} + \frac{e}{c}\underline{\sigma}\cdot\underline{H}\right)\psi = 0$$

Dirac equation

$$\left[\left(i\frac{\partial}{\partial t} - V\right)^2 - c^2\left(\underline{\alpha}\cdot\left(\underline{p} - \frac{e}{c}\underline{A}\right)\right)^2 - m^2c^4\right]\psi = 0$$

$$\left((E - V)^2 = c^2(p - eA)^2 + m^2c^4\right)$$

Dirac $\rightarrow$ K.-G. if no external field.

Test for motion in [illegible]

[illegible] for the energy term of the form $\frac{p^2}{2m}$,

[illegible] μ [illegible] magnetic moment.

If magnetic moment [illegible] field [illegible] [illegible]

[illegible] energy [illegible] without H, then [illegible] E [illegible]

[illegible] E_0 [illegible] then [illegible] satisfying [illegible]

[illegible] E_0 satisfies [illegible] energy [illegible] E

this can be done if $V \ll E$ i.e. $V \ll mc^2$ -

then $(E-V)^2 - (E_0-V)^2 \cong E^2 - 2EV - E_0^2 + 2E_0V$

$\cong E_0(E-E_0) + 2E_0$

$\sim (E-E_0) \cdot 2E_0$

$(E-E_0)\,2E_0 = -\frac{e\hbar}{2mc}\,\sigma \cdot H$.

$E - E_0 = -\frac{e\hbar}{2E_0}\,\sigma \cdot H$

[illegible] magnetic [illegible] moment [illegible] of [illegible]

is $\mu_- = -\frac{e\hbar}{2E_0}\,\sigma$

for non-relativistic — $E_0 \sim mc^2$,

$\mu = -\frac{e\hbar}{2mc}\,\sigma$

σ_z has eigenvalue $+1$, -1 [illegible] σ_z has eigenvalue

[illegible] $\pm\frac{e\hbar}{2mc}$

Ratio of mag. mom. to ang. mom. is $\frac{e\hbar}{2mc} : \frac{e}{mc}$

this is twice as great as gyromagnetic ratio for orbital motion — $\frac{\text{magnetic}}{\text{ang. mom.}} = \frac{e}{2mc}$ for orbital motion

Pauli Kramers Heisenberg
Van Vleck Uhlenbeck
Goudsmit

Corben + Blatt
Kemble

(from 8) 2nd order Dirac eq'n:

$$\left[\left(i\hbar\frac{\partial}{\partial t} - V\right)^2 - c^2\left(-i\hbar\,\text{grad} - \frac{e}{c}\underline{A}\right)^2 - m^2c^4 + e\hbar c\,\underline{\sigma}\cdot\underline{H} - ie\hbar c\,\underline{\alpha}\cdot\underline{E}\right]\psi$$

The two smaller Dirac f'ns are to larger ones $\sim \sqrt{\frac{E - mc^2}{mc^2}}$

Hence for $E \sim mc^2$, can neglect two small comp's.

write ψ as two row matrix : $\psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix}$

$\phi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$ — small comp's.

$\chi = \begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix}$ - large comp's

then $\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}$ $\quad \underline{\sigma} = \begin{pmatrix} \underline{h} & 0 \\ 0 & -\underline{h} \end{pmatrix}$

$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Then Dirac eq'n becomes:

$$(E - V)\psi = \alpha\cdot(cp - eA)\psi - \beta mc^2\psi$$

$$\therefore \quad (E - V)\phi = \sigma\cdot(cp - eA)\chi - mc^2\phi$$

$$(E - V)\chi = \sigma\cdot(cp - eA)\phi + mc^2\chi$$

or: $(E + mc^2 - V)\varphi = \sigma\cdot(cp - eA)\chi$

$(E - mc^2 - V)\chi = \sigma\cdot(cp - eA)\varphi$

if $E \sim mc^2$:

V small: $(2mc^2/\hbar)\varphi = \sigma\cdot(-i\hbar c\,\mathrm{grad} - eA)\chi$

$$\varphi = -\sigma\cdot\frac{(i\hbar\,\mathrm{grad} + eA)\chi}{2mc^2}.$$

$\therefore$ 2nd order eq'n gives:

$$\left((E-V)^2 - c^2(i\hbar\,\mathrm{grad} + eA)^2 - m^2c^4 + e\hbar c\,\sigma\cdot\underline{H}\right)\chi = i\hbar c\,\sigma\cdot E\,\chi$$

$$= i\hbar c\,E\cdot\sigma\,\varphi$$

$$= i\hbar c\,E\cdot\sigma\frac{(-\sigma\cdot(i\hbar\,\mathrm{grad} + eA))\chi}{2mc^2}$$

neglecting A: $\quad = +\frac{e\hbar^2}{2m}E\cdot\sigma\,\sigma\cdot\mathrm{grad}\,\chi$

can show that:

$$(E\cdot\sigma)(\underline{\sigma}\cdot\mathrm{grad}\,\chi) = \underline{E}\cdot\mathrm{grad}\,\chi + i(\sigma\times E)\cdot\mathrm{grad}\,\chi$$

$$= E\cdot\mathrm{grad}\,\chi + i\,\underline{\sigma}\cdot(\underline{E}\times\mathrm{grad}\,\chi)$$

if electric field, $\varphi = \varphi(r)$,

$$\underline{E} = -\frac{\partial\varphi}{\partial r}\frac{\underline{r}}{r}.$$

and 2nd term above is

$$\frac{1}{r}\frac{\partial\varphi}{\partial r}\,\sigma\cdot\underline{r}\times\mathrm{grad}\,\chi$$

But orbital mom. $= \underline{r}\times\underline{p} = \underline{r}\times\hbar\,\mathrm{grad}$

$\therefore\ \sigma\cdot\underline{r}\times\mathrm{grad}\,\chi$ is spin-orbit interaction

$$\frac{1}{r}\frac{\partial\varphi}{\partial r}\,\sigma\cdot\underline{M}\,\chi$$

In nuclei, forces are non central mostly, - electric & magnetic effect are small. But still get the somewhat interesting because of Thomas effect - due to accel. of particle - effect is negative of that for case when field is present. I.e. in [But apparently not sufficient to cause splitting of ground state of He^5].

$$\therefore \left[(E-V)^2 + c^2\left(\text{grad} - \frac{ie}{c}A\right)^2 - m^2c^4 + e\hbar c\,\underline{\sigma}\cdot\underline{H} - \frac{e\hbar^2}{2m}\left(E + i(\sigma\times E)\right)\cdot\text{grad}\right]\chi = 0$$

for central field $E = -\frac{1}{r}\frac{\partial\varphi}{\partial r}\,\underline{r}$

$$E\cdot\text{grad}\,\chi = -\frac{1}{r}\frac{\partial\varphi}{\partial r}\,\underline{r}\cdot\text{grad}\,\chi$$

$$= -\frac{\partial\varphi}{\partial r}\frac{\partial\chi}{\partial r}.$$

$$\therefore \left[(E-V)^2 + c^2\left(\text{grad} - \frac{ie}{c}A\right)^2 - m^2c^4 + e\hbar c\,\underline{\sigma}\cdot\underline{H} - \frac{dV}{dr}\left(-\frac{\hbar^2}{m}\frac{\partial}{\partial r} + \frac{\hbar}{2m}\frac{i}{c}\,\sigma\cdot\underline{M}\right)\right]\chi$$

if $E = mc^2 + W$

$$(E-V)^2 - m^2c^4 = (W - V + mc^2)^2 - m^2c^4$$

$$= (W-V)^2 + 2mc^2(W-V)$$

small relativistic perturbation

$$\therefore \left[W - V + \frac{\hbar^2}{2m}\left(\text{grad} - i\frac{e}{\hbar c}A\right)^2 + \frac{(W-V)^2}{2mc^2} + \frac{e\hbar}{mc}\,\underline{\sigma}\cdot\underline{H} - \left(\frac{\hbar}{mc}\right)^2\frac{dV}{dr}\left(-\frac{\partial}{\partial r} + \frac{e\hbar}{2c}\,\sigma\cdot\underline{M}\right)\right]$$

1st 3 terms give Schrödinger eqn; remaining terms are small perturbations.

~~[illegible] terms [illegible] grad~~

(mult)

$$\left(W - V + \frac{\hbar^2}{2m}\nabla^2\right)\chi = \frac{ie\hbar}{mc} A\cdot\text{grad}\,\chi$$ I interaction, ext. mag. field w orbital mom. - Zeeman effect (paramagnetic)

$$+\frac{e^2}{2mc^2}A^2\chi$$ I important if no magnetic moment - gives rise to diamagnetism (Landau levels)

$$-\frac{(W-V)^2}{2mc^2}\chi$$ - relativistic correction. (without spin) always lowers eigenvalue

Pauli - $$-\frac{e\hbar}{2mc}H\cdot\sigma\chi$$ spin - external mag. field interaction

(see Dirac) $$+\left(\frac{\hbar}{2mc}\right)^2\frac{\partial V}{\partial r}\frac{\partial\chi}{\partial r}$$ gives interaction only for s electrons, replaces relativ. spin-orbit theory.

explains fine structure (except $$+\left(\frac{\hbar}{mc}\right)^2\frac{1}{r}\frac{\sigma\cdot M}{r}\chi$$ spin-orbit interaction

$L = \frac{M}{\hbar}$ $$= +\left(\frac{\hbar}{mc}\right)^2\frac{\partial V}{\partial r}\frac{\sigma\cdot L}{r}\chi$$

9/41 $$\chi = \chi(r)\begin{pmatrix}\Psi_\ell^{m-1/2}\\ \Psi_\ell^{m+1/2}\end{pmatrix}.$$

Pauli, Zeit. f. Phys. 43 [illegible]
Bethe, Handbuch 24/1, 304

For states of total ang. mom. j,

$$2L\cdot S = j(j+1) - \ell(\ell+1) - s(s+1);$$

$$s = 1/2,\quad j = \ell \pm 1/2,$$

$$2L\cdot S = \begin{cases}\ell\\ -(\ell+1)\end{cases}$$

Coulomb field $V = -\frac{e^2}{r}$

$$\frac{1}{r}\frac{\partial V}{\partial r} = \frac{e^2}{r^3}$$

$\therefore$ 1st order correction is: $\left(\frac{\hbar}{mc}\right)^2 \frac{e^2}{2}\begin{pmatrix} l \\ -(l+1) \end{pmatrix} \overline{r^{-3}}$

$$\overline{r^{-3}} = \frac{1}{n^3(l+1)(l+\frac{1}{2})l\, a_0^3} \qquad a_0 = \text{Bohr radius}$$

if $l = 0$, $j = \frac{1}{2}$, $s = \frac{1}{2}$, $L \cdot S = 0$

and $\overline{r^{-3}}$ diverges for s-states.

$\therefore$ for $l = 0$ correction is indeterminate.

$\therefore$ go back to derivation; instead of $(2mc)^2$ in denominator, should have: $(2mc - \frac{V}{c})^2$ but

$-V \sim \frac{1}{r}$ $\therefore$ for small r integrand is actually $\frac{r^{-3}}{r^{-1}} = r^{-1}$ & converges even for s-states.

$\therefore$ spin-orbit interaction is zero, in contradiction to experiment. other term: $\left(\frac{\hbar}{mc}\right)^2 \frac{dV}{dr}\frac{\partial \chi}{\partial r}$

gives: $\int \frac{e^2}{r^2}\chi \frac{\partial \chi}{\partial r} \cdot 4\pi r^2 dr = \frac{1}{2}\chi^2 \Big|_0^\infty$

which gives contribution only for s-states — (only s states are not zero at origin). turns out that this gives same result as if l's were cancelled above.

This is OK only for Coulomb field)

$j = l + \frac{1}{2}$ is raised, $l - \frac{1}{2}$ is lowered by spin-orbit interaction

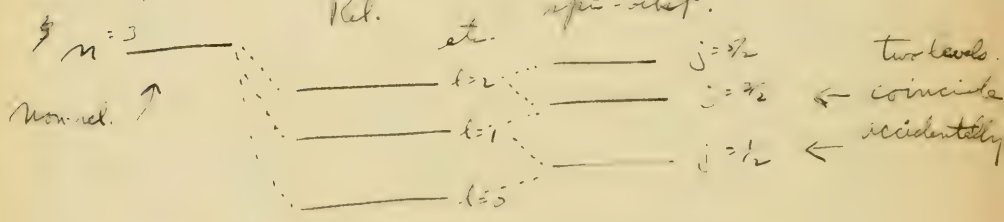
Relativistic correction $-\frac{(W \cdot U)^2}{mc^2} = \frac{(W + \frac{e^2}{r})^2}{mc^2}$ greatly increasing

for wave functions concentrated near origin – i.e. for small l.

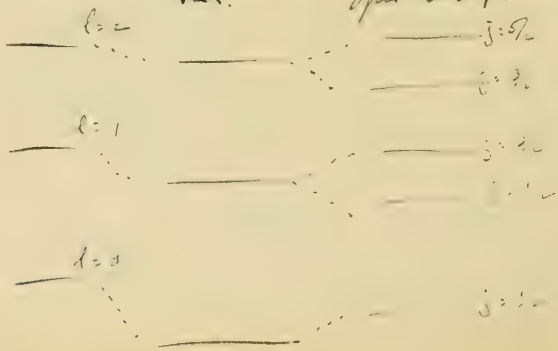
Wholly relativistic : $-\frac{1}{2}\alpha^2 \frac{Ry}{n^3}\left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right)$ $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$

$\nu \sim \frac{1}{20,000}$ of freq. of H lines.

spin-orbit interaction : $\frac{1}{4}\alpha^2 \frac{Ry}{(l+\frac{1}{2})n^3}\begin{pmatrix} l+1 \\ -l \end{pmatrix}$



But in Alkali l-levels are already separated, non-relativistically



With nucleus Z, dimensions of wave f'ns are reduced in the ratio Z; $\therefore$ $\overline{r^{-3}}$ is multiplied by Z^3, V & $\frac{\partial V}{\partial r}$ by Z; and rel. & sp-orbit interactions are all multiplied by Z^4.

$\therefore$ fine structure becomes much larger -

In X-ray spectra, inner electrons move almost in Coulomb field, $\therefore$ almost the same fine structure as H, only ~~[illegible]~~ small "screening constants" - Z-σ effective nuclear charge -

But relativistic effect much larger -

Formula of

$-d_{5/2}$

$-d_{3/2}$

"relativistic doublet" $\left\{ \begin{array}{l} -p_{3/2} \\ -p_{1/2} \end{array} \right.$

"screening doublet" $\left\{ \begin{array}{l} -p_{1/2} \\ -s_{1/2} \end{array} \right.$

Pauli theory can't calculate energies to order α^4

Can get wave functions to order α^2 - useful for intensities of alkali spectra.

Doublet lines should have intensity ratio 2:1 for p-s transition (statist. wt. for $j = 3/2 = 2j+1 = 4$, $j = 1/2$, $2j+1 = 2$) this is well followed in K_α, K_β, fairly well in K_γ not well in L_α;

necessary to use relativistic wave f'ns instead of 1st order -

Fermi Zeitsch. f. Phys. 1932 v

Direct solution of Dirac eq. in presence of central field.

Dirac - Proc. Roy. Soc.
Darwin, Gordon, Swanson

get the old formula for levels -
fine structure formula

Nov 11'41 An atom lacking one atom of a complete shell has same energy levels as one with one atom in full shell, considering electrostatic interaction. But spin-orbit interaction inverts doublets. In general, "inverted multiplets" when std of mult j lies lowest.

Levels of a multiplet are $A + 2B\,\underline{l}\cdot\underline{s} = A + B[j(j+1) - l(l+1) - s(s+1)]$

and $E_j - E_{j-1} = 2Bj$ Landé interval rule -

e.g. ^4D: $3/2$ — ↑ 1
$5/2$ — ↑ 5
$7/2$ — ↑ 3
$J = 3/2$

But interval rule breaks down in He, Li^+ because field deviates strongly from central field
Heisenberg first not quite correctly, then Breit correctly calculated fine structure for 2^3P, e.g.:

— $J = 0$
═ $J = 1$
$J = 2$

Inverted multiplet
no interval rule;
ratio 7:1 instead of 2:

magnetic interaction between spins of two electrons of form:
$\left(\frac{s_1 \cdot r\, s_2 \cdot r}{r^2} - \frac{1}{3} s_1 \cdot s_2\right)$ which always gives a splitting.

— $l-1$
═ $l+1$
— l

then also reducing spin-orbit:

— $l+1$
— l
— $l-1$

actual levels are combination of both

Alkali abnormalities: d states of Rb are inverted due to exchange between d electron + some s electrons.

Negative energy levels. Free electron: $E = \pm c\sqrt{p^2 + m^2c^2}$

(classically can forget negative energies, since if energy is initially +, it remains + forever). Q.M.:

$$E\psi = c\,\alpha\cdot p\,\psi - \beta mc^2\psi$$

$$\frac{E}{c}\psi_1 = p_x\psi_4 - ip_y\psi_4 + p_z\psi_3 - mc\,\psi_1$$
$$\psi_2 = (p_x + ip_y)\psi_3 - p_z\psi_4 - mc\,\psi_2$$
$$\psi_3 = (p_x - ip_y)\psi_2 - p_z\psi_1 + mc\,\psi_3$$

If $\psi_4 = 0$: $\left(\frac{E+mc^2}{c}\right)\psi_1 = p_3\psi_3$

$$\therefore \quad \psi_2 = (p_x + i p_y)\,\psi_1$$

$$\frac{E-mc^2}{c}\,\psi_3 = (p_x - i p_y)\,\psi_2 + p_3\,\psi_1$$

$$\left(\frac{E+mc^2}{c}\right)\left(\frac{E-mc^2}{c}\right)\psi_3 = \left[(p_x - i p_y)(p_x + i p_y) + p_3 p_3\right]\psi_3$$

$$\therefore \quad E^2 - m^2c^4 = c^2p^2 \quad \text{— so this is a sol}^{n}$$

$$1 = \sum_{i=1}^{3} |\psi_i|^2 = |\psi_3|^2\left(\frac{c^2p^2}{(E+mc^2)^2} + 1\right) = |\psi_3|^2\left[\frac{c^2p^2 + (E+mc^2)^2}{(E+mc^2)^2}\right] \cong \frac{2E}{E+mc^2}$$

$$\therefore \quad \psi_3 = \sqrt{\frac{E+mc^2}{2E}}.$$

sol'ns:

$$\frac{1}{\sqrt{2E(E+mc^2)}}\begin{pmatrix} cp_3 \\ c(p_x+ip_y) \\ E+mc^2 \\ 0 \end{pmatrix} \qquad \frac{1}{\sqrt{\ }}\begin{pmatrix} c(p_x-ip_y) \\ -cp_3 \\ 0 \\ E+mc^2 \end{pmatrix}$$

$$\frac{1}{\sqrt{2E(E-mc^2)}}\begin{pmatrix} cp_3 \\ c(p_x+ip_y) \\ -E+mc^2 \\ 0 \end{pmatrix} \qquad \frac{1}{\sqrt{\ }}\begin{pmatrix} c(p_x-ip_y) \\ -cp_3 \\ 0 \\ -E+mc^2 \end{pmatrix}$$

positive E : ψ_3, ψ_4 large $\qquad \sum_k \psi_k^{*}\psi_k' = 0$

negative E : ψ_1, ψ_2 large

Dirac assumed all negative energy states filled by Pauli principle; (Fermi statistics necessary therefore). + positive energy electrons appear act as they should; + can't go to negative states; but the reverse may happen; electrons negative states may absorb photon + go to positive state, leaving a hole which acts like a positive charge. Dirac at first thought it was proton; but opposite should act exactly like electron except for charge. Anderson in 1933 observed positrons; Blackett + others observed "pair formation" by the C" γ-rays 2.6 c MeV cosmic rays + measured mass from : $W_+ + W_- = h\nu - 2mc^2$ + it was right

Jan 14/41 Radiation theory: Expand potentials in Fourier series in big box of dimension $\Omega = L^3$

Then $\underline{A} = \sum_{\underline{k}} \underline{a}_k e^{i\underline{k}\cdot\underline{r}}$ $\qquad k_x = \frac{2\pi}{L} n_x$ $\quad n_x$ an integer (similarly y

since A is real, $\underline{a}_{\underline{k}} = \underline{a}^*_{\underline{k}}$

No of normal modes $= \left(\frac{L}{2\pi}\right)^3 dk_x\, dk_y\, dk_z = \frac{\Omega}{(2\pi)^3} d\underline{k}$.

In absence of charges & currents, $\Box^2 \underline{A} = 0$;

$\therefore + \frac{1}{c^2}\frac{\partial^2 a_k}{\partial t^2} = -k^2 a_k$

I field free case:

$$\mathcal{H} = \frac{1}{8\pi}\int (E^2 + H^2)\, d\tau \qquad \therefore a_k \sim e^{\pm i\omega t} \qquad \omega = ck.$$

Heisenberg & Pauli considered field equals at real part; one gets commutation relations like $[E(1), H(1')] \sim \delta(1-1')$; gets quite complicated – Dirac & later Fermi. Fourier expansion – this theory can do all that $\underline{H} = \underline{P}$ theory does, only more simply –

Expand: $\quad \phi = \sum \varphi_k e^{i\underline{k}\cdot\underline{r}}$, $\quad H = \operatorname{curl} A = \sum i\underline{k}\times\underline{a}_k e^{i\underline{k}\cdot\underline{r}} = \sum i\underline{k}\times$

$$\underline{E} = -(\nabla\phi + \tfrac{1}{c}\dot{\underline{A}}) = -\sum\left(\tfrac{1}{c}\dot{a}_k + i\underline{k}\varphi_k\right) e^{i}$$

Then $H^2 = \sum_{k\,l'} \sum i(\underline{k}\times\underline{a}_l) e^{i\underline{k}\cdot\underline{r}} \sum -i(\underline{l}'\times\underline{a}^*_{l'}) e^{-i\underline{l}'\cdot\underline{r}}$

$$= \sum_{k\,l'}\sum (\underline{k}\times\underline{a}_l)(\underline{l}'\times\underline{a}^*_{l'}) e^{i(\underline{k}-\underline{l}')\cdot\underline{r}}$$

$$E^2 = \sum_{l,l'}\Big[\tfrac{1}{c^2}\dot{a}_l\dot{a}^*_{l'} + \underline{l}\cdot\underline{l}'\varphi_l\varphi^*_{l'} - \tfrac{i}{c}(\dot{\underline{a}}_{l'}\cdot\underline{l}'\varphi^*_{l'} - \dot{\underline{a}}^*_{l'}\cdot\underline{l}\,\varphi_l)\Big] e^{i\underline{l}}$$

Integrate over box $L^3 = \Omega$ all integrals with $k \neq k'$ will $= 0$, if $k = k'$ get volume $\int$

$$\therefore \frac{1}{8\pi}\int (E^2 + H^2)\, d\tau = \frac{\Omega}{8\pi}\sum_k |\underline{k}\times\underline{a}_k|^2 + k^2|\varphi_k|^2 + \frac{|\dot{a}_k|^2}{c^2} + \frac{1}{c^2}\dot{\varphi}_k\varphi^*_k$$

Note that $\operatorname{div} A = \sum i\underline{k}\cdot\underline{a}_l e^{i(\underline{k}\cdot\underline{r})}$

and $\operatorname{div} A = -\frac{1}{c}\dot{\phi}$]

$\therefore \operatorname{div} A = \sum \varphi_k e^{i\underline{k}\cdot\underline{r}}$

$\therefore -\frac{1}{c}\dot{\varphi}_k = i\underline{k}\cdot\underline{a}_k$

[illegible]

Read Fermi [illegible]

[illegible]

Introduce polarization,

$$b_{k_j} = \frac{1}{c}\sqrt{\frac{\Omega c}{4\pi}}\, a_{k_j} \;;\quad \mathcal{H} = \frac{1}{2}\sum c^2 k^2 b_{k_j}^2 + \dot{b}_{k_j}^2$$

$$p_{k_j} = \bar{u}_{k_j} \quad \text{where}$$

$$\ddot{b}_{k_j} = \dot{p}_{k_j} = -\frac{\partial \mathcal{H}}{\partial b_{k_j}} = -c^2 k^2 b_{k_j}$$

Jan 1641

$\frac{\Omega}{(2\pi)^3}\, d\underline{k}$ normal modes ; $\quad \mathcal{H} = \frac{\Omega}{8\pi}\sum k^2 a_k^2 + \frac{1}{c^2}\dot{a}_k^2$

$$b_k = \sqrt{\frac{\Omega}{4\pi}}\,\frac{a_k}{c} \qquad \text{then} \quad \mathcal{H} = \frac{1}{2}\sum \omega_k^2 a_k^2 + p_k^2 \qquad \omega_k = ck .$$

$$p_k = \dot{b}_k$$

(really $\dot{b} = \frac{\partial \mathcal{H}}{\partial p_k} = p_k^*$

$$\underline{A} = c\sqrt{\frac{4\pi}{\Omega}}\sum_k b_k e^{i\underline{k}\cdot\underline{r}}$$

that b's are coord's, p's are momenta.

Hamiltonian is separable.

then solution $\Phi = \prod_k \varphi(b_k)$.

Each φ satisfies : $\frac{\hbar^2}{2}\frac{\partial^2 \varphi_k}{\partial b_k^2} + \left(E - \frac{1}{2}\omega_k^2 b_k^2\right)\varphi = 0$

Where $\varphi = H_{n_k}(b_k)$ $\quad E_k = (n_k + \frac{1}{2})\hbar\omega_k$

$$\therefore E = \sum E_k = \sum_k \hbar\omega_k (n_k + \tfrac{1}{2})$$

If all n's are zero, no radiation $\quad E = \frac{1}{2}\sum \hbar\omega_k$ which is infinite

I repeat, [illegible] only energy changes. But in detail any energy has quantized [illegible] this again not a serious, since [illegible] force would be zero, since the energy density is the same everywhere. Anyhow it can be shown that by using [illegible] $(E+iH)(E-iH)$ [illegible] E^2+H^2 or [illegible] Hamiltonian. Serious difficulties [illegible] with neg. energies — infinite energy [illegible]

If we have j particles: (electrons)

j, s_j, l_j are Dirac [illegible] + position of jth elec.

$$H_f = \sum_j \underbrace{c\,\alpha_j\cdot p_j - mc^2\beta_j + V(r_j)}_{\text{electron}} + \underbrace{\tfrac{1}{2}\sum_k \omega_k^2 b_k^2 + p_k^2}_{\text{radiation}} - \underbrace{\sum_j e\,\alpha_j\cdot A(r_j)}_{\text{interaction}}$$

But $A = c\sqrt{\frac{4\pi}{\Omega}}\sum_k b_k e^{ik\cdot r}$

$\therefore$ Interaction is: $-ec\sqrt{\frac{4\pi}{\Omega}}\sum_j \alpha_j\cdot\sum_k b_k e^{ik\cdot r_j}$

(b's commute with all [illegible] concerning electrons)

Wave fn with r_j $F(r_j, b_k)$

Without interaction $F = \Psi(r_j)\,\Phi(b_k)$.

M: state of electrons

n_k: state of field oscillators

In general Ψ not separable because of elect. interactions

Transition probabilities for small times are: $\int F^*_{final}\,(\text{interaction})\,F_{initial}\,d\tau_M\,d\tau_L$

$\downarrow$ b_k in 1st approx.

Since F contains $\prod_k \varphi_{n_k}(b_k)$, we must have $n_{k'}^{final} = n_{k'}^{initial}$ $k' \neq k$

$n_k^{final} = n_k^{initial} \pm 1$ $k' = k$.

i.e. to get a transition one n_k changes by one unit. Then $\int b_k\,\varphi_{n_k}^{final}\,\varphi_{n_k}^{initial}\,d\tau_k = \sqrt{\frac{1}{2}\frac{\hbar}{\omega_k}}\,\sqrt{n}$

$\therefore (\cdots n_k \cdots | H_{int} | \cdots n_k - 1 \cdots) = -ec\sqrt{\frac{4\pi}{\Omega}}\cdot\sqrt{\frac{2\pi\hbar}{\omega_k}\,n_k}\cdot\sum_j \alpha_j\,e^{ik\cdot r_j}$ $\quad$ α_j is comp. of α_j in direction of $\alpha_j\cdot u_k$

$(\cdots n_k \cdots | H_{int} | \cdots n_k + 1 \cdots) = \;-\;-\;-\;\cdot\sqrt{(n_k+1)}$

Complete matrix element: $\sum_j \int \Psi^*_{final}\,\alpha_j\cdot u_k\,e^{ik\cdot r_j}\,\Psi_{initial}\,d\tau_M$ Without approximation, this is just the sum of the matrix of all electrons. Retardation factor $e^{ik\cdot r_j}$.

Dipole radiation: $\int \psi_f^*\sum_j \alpha_j\,\psi_i\,dx = \frac{i}{\hbar c}(E_f - E_i)\int \psi_f^*\sum_j r_j\,\psi_i$ since α is matrix with [illegible]

Recall Heisenberg $\rightarrow$ [illegible]

In evaluating matrix elements expand $e^{i\underline{k}\cdot\underline{r}}$ not in power series, but in spherical harmonics : $e^{i\underline{k}\cdot\underline{r}} = \frac{1}{\sqrt{2}} \sum i^l J_{l+\frac{1}{2}}(kr) P_l(\theta)$

l^{th} term gives rise to $\begin{cases} \text{electric } 2^{l+1} \text{ pole} \\ \text{magnetic } 2^l \text{ pole} \end{cases}$ (see Heitler's paper)

(this arises from consideration of transformation properties of spherical harmonics)

electric 2^{l+1} pole from l $l+2$ ($\tau_{l+\frac{1}{2}}$ $\tau_{l+\frac{3}{2}}$); magnetic 2^l-pole from l $J_{l+\frac{1}{2}}$

for $kr \ll 1$: $\frac{J_{l+\frac{1}{2}}}{\sqrt{r}} \sim (kr)^l$.

Dipole : $\frac{e_i \cdot e_f}{i\hbar} \int \psi_f^* x \psi_i$ this also from classical theory. Selection rules : l can change by one unit; also 1 unit change in field selection. Electric 2^{l+1} pole : $|\Delta s| = l+1$ parity unchanged by $(-1)^{l+1}$
magnetic 2^l-pole $\Delta s = l$ . . . . . .

Non-relativistic H/H. : $\underline{p}$ replaced by $\frac{\hbar}{i}\underline{\nabla}$ grad (velocity = momentum).

Radiation processes : classified according to no. of quanta involved.

One quanta : absorption + emission ; interaction theory gives probability per unit time of : $\frac{2\pi}{\hbar} |\text{Matrix el.}|^2 \cdot N_\sigma$ of final state, resonant energy.

Emission : No. of final states ; $\frac{\Omega}{(2\pi)^3} d\underline{k} = \frac{\Omega}{8\pi^3} 4\pi k^2 \frac{dk}{dE} = \frac{\Omega}{8\pi^3} \frac{4\pi k^2}{\hbar c}$.

but two directions of polarization ($\therefore \times 2$) but non-relativistic rule determines polarization for a given transition – this must also be considered.

$\therefore$ trans. prob. $\sim k^2 |\text{matrix el}|^2 \sim \omega^2 \cdot \frac{1}{\omega} |\text{current}|^2 = \omega |\text{current}|^2$ (Ω cancels out as it must)

$\sim \omega^3 |\text{dipole moment}|^2$

Intensity $= \hbar\omega$ emission prob. $\sim \omega^4$.

Absorption : Final state of material system in continuum. Assume $n \neq 0$ for one ν only one rad. oscillator. [No. of final states of material system/energy] $\cdot \frac{1}{\omega} \cdot \frac{n}{\Omega} |\text{current}|^2 \sim$ abs. prob. Introduce Rad. density $= \frac{n\hbar\omega}{\Omega}$

then prob. $\sim \frac{\rho}{\omega^2} |\text{current}|^2$ (No. of states) $\sim \rho |\text{dipole}|^2 N(E)$. [$\rho \sim \frac{1}{\lambda^3} \sim \omega^3$].

(matrix derived also from both absorption + emission on statistical basis)

Ind. = induced emission ; total emission = induced + spontaneous

First state discrete: simple to calculate only if there is a continuous distribution radiation energy -- see use of quantum physics, not energy - i.e. assume an average in fr states in region; ~~Let's abs. ...~~ otherwise must know the width of levels involved. Then abs. prob. $\sim \frac{c}{(\nu-\nu_0)^2+\frac{1}{2}\gamma^2}$ γ: natural width (of the 2 states) natural spectrum

Emission, really has this shape too] · Weisskopf + Wigner, 1932 ~ Z. f. Ph.

Jan 21 '41 E_1: electron energy before $E_1 = E_2 + \nu$ - [illegible]

E_2: " " after: $p_1 = p_2 + \frac{\nu}{c}$, or $\nu = c(p_1 - p_2)$

$\nu^2 = c^2(p_1-p_2)^2 = (E_1-E_2)^2$

$\therefore (E_1-E_2)^2 - c^2(p_1-p_2)^2 = 2c^2 p_1 p_2(1-\cos\theta)$

$\therefore c^2(p_1-p_2)^2 + 2c^2 p_1 p_2(1-\cos\theta) = (E_1-E_2)^2$

$\underbrace{E_1^2 - c^2 p_1^2}_{m^2c^4} + \underbrace{E_2^2 - c^2 p^2}_{m^2c^4} - 2E_1E_2 + 2c^2 p_1 p_2 = 2c^2 p_1 p_2(1-\cos\theta)$

Lorentz transformation to make $p_2 = 0$:

then $c^2 p_1^2 = (E_1-E_2)^2$

$E_1^2 - m^2c^4 = (E_1-E_2)^2$

$(E_1+mc^2)(E_1-mc^2) = (E_1 \pm mc)^2$.

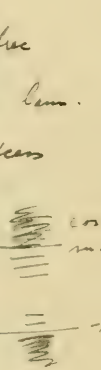
$(E_1 - mc^2) \cdot 2mc^2$

or $(E_1+mc^2) \cdot 2mc^2$

Can calculate cross-sections

{absorption} or {emission} are quantum by free electron - can't satisfy momentum cons.

must have nucleus to take up excess momentum -



In a field of force:

Possible transitions:

1) Discrete - discrete: $\Delta E < mc^2$ possible

nonrelativity - no Sch. or Pauli f'ns. or states within limits for Tritium

dimensions of system ~ λ_c ~ $\frac{h}{mc}$ or $\frac{h}{\sqrt{mV}}$ ~ $\sqrt{\frac{V}{mc^2}} < 1$ $\therefore$ retardation negligible. (e^{ikr}) $\therefore$ nac

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2) Continuous - discrete: ~~absorption~~ emission; also recombination (ion absorbs + becomes stay) (rare) $\sigma \sim 10^{-20}$ cm. (scattering $\sim 10^{-16}$).

absorption: photoelectric effect. $\sim Z^4 \nu^{-3}$ bigger for more strongly bound atoms. also become with

becomes upper state becomes more nearly free electron state -

angular distribution: $\sim \sin^2\theta$ for low energies - (s elec) p elec: $\sim \sin^2\theta \cdot 1$

higher energies: $\sin^2\theta(1+\alpha\frac{v}{c}\cos\theta)$; higher energy - more + more in forward direction

actually fluctuation effect becomes ... $\nu^{-3.5}$ ... $5 E_B < h\nu < mc^2$

$5'$ $\quad mc^2 < h\nu$

c. interaction - retardation - quite use in relativity expansion

nuclear field. continuous x-ray spectrum. electron can emit energy only by producing one, one by the process.

Coulomb field!

ordinary x-ray tubes: 10-100 kev, fraction of energy going into x-ray $\sim \frac{E}{\epsilon}$ ~(electron energy) $\quad \epsilon \sim \frac{\alpha^2 mc^2}{Z}$.

$\therefore$ 100 k.v. electron use about 1% of the energy producing x-rays in heaviest elements

(higher energies again better yields). energy loss ... $\frac{mc^2}{\alpha^2 Z}$ $\quad E$

In Stars, very important -

Jan 23 '41 hole left in negative energy states when an electron is removed, acts just like positive electron, with $-E$ energy of hole $-p$ momentum etc.

pair production: $h\nu = E_- + E_+$ $\quad E_0$ ... mc^2 ... $-mc^2$ ... $-E_-$

$p_\nu \neq p_- + p_+$ (non-conservation of momentum to atom)

probability should be in principle calculated from matrix elements: but complexity of wave functions make it hard. Some approximate (numerical) calculations: Heitler + Jaeger $Z=87$ high

Some approximations by: $\psi = \psi_{free} + \text{perturbation}$ - use Born approx. $\sim c^2 Z$

(1st order wave fn - used to calculate matrix element:

Detailed:

e: interaction between electron + field

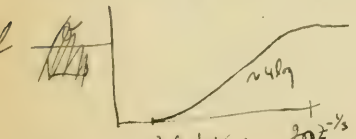
$e^2 Z$: " " " + atom.

$\therefore \sigma \sim e^6 Z^2$;

to have dim. cm^2, we must have:

$$\sigma \sim \frac{e^2}{\hbar c} Z^2 \left(\frac{e^2}{mc^2}\right)^2 f\left(\frac{h\nu}{mc^2}\right)$$

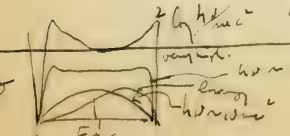
Turns out that $f\left(\frac{h\nu}{mc^2}\right) \sim 1$ for $\frac{h\nu}{mc^2} \sim 1$.



Bethe + Heitler P.R.S. 1934

main contribution comes from region $\frac{\hbar}{mc} < r < \frac{\hbar}{mc}\frac{h\nu}{mc^2}$.

(radius of atom $= a_0 Z^{-1/3}$
$= \frac{\hbar}{mc} \cdot 137 Z^{-1/3}$.)



This doesn't take into account coulomb repulsion of positron + attraction of electron by nucleus

low energy photons had to wait —

Hulme & Jaeger results good.

$\gamma - ih - c^2$ — $h\nu = 2.0$ Mev — β not at the. $h\nu = 10$ Mev. Coming γ ionizing ionization 20% diff which is pile of objections

Pair production: annihilation of pair & creation of photon. Only possible if a neg. state empty. Not to be by —

Two quantum processes. (Better think positron's lamification post)

Φ simultaneous absorption of two (unoccupied) Pair creation — really 1st order)

emission ⟶ important for creation holes. states

Scattering (one in, one out). of course higher corrections. impossible in pair

... must imp. lines. one gets expressions like these: $\sum_{\text{intern.}} \frac{H_{in,int.} H_{int.\,fin.}}{E_{int} - E_{int}}$

If $h\nu \sim mc^2$, take H: dipole interaction.

neglect other interaction ($e^{ikx} = 1$)

and $k \to x$

Thus we get the dispersion formula: (Kramers & Heisenberg, before Q.M.)

$$\Phi_{mn} \text{ (transition amplitude)} \sim \sum \frac{\lambda_{m,k}\,\lambda_{k\,m}}{E_n + h\nu - E_k} + \frac{\cdots}{E_n - h\nu - E_k}$$

(i.e. int. ... int.)

$h\nu \gg$ binding energies.

If only positive E_k are intermediate states, Φ = amp. ... d.

but state $E_k = -mc^2$ give large contribution if the element ... $\sim \frac{e}{mc^2}$

Φ (hole theory): Φ^2 gives main contribution to scattering for large $h\nu$. (Dirac theory)

X-ray scattering — one gets form factors $\int \rho(\mathbf{r})\, e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}}$

if also gives incoherent scattering (Raman Compton). $\int \rho_m \sum_j e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_j}$

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m 25, '40 | Compton effect. $E = 2h\nu(1 - \cos\theta)\,\frac{h\nu}{mc^2}$ if $h\nu \gg mc^2$,

$\Delta\lambda = 2\frac{h}{mc}(1 - \cos\theta)$ $\lambda_{min} = \frac{h}{2mc}$

and $\nu_{max} = \nu$ incident.

For very high energy γ-rays, electrons, neutrinos, heavy mesons, neutrons, energy very high.

Kinetic expression to dispersion: $\sum \frac{\lambda_{nk}\lambda'_{kn}}{\cdots} + \frac{\lambda'_{nk}\lambda_{kn}}{\cdots}$

pairs for scattered [illegible] ; α comp. of α in dir. of polarization.

$$\alpha_{nk} = \int \psi_n^* e^{-i\underline{k}\cdot\underline{r}} \alpha_p \psi_k \, d\tau$$

take $\psi_n = u_n e^{\frac{i}{\hbar}\underline{p_n}\cdot\underline{r}}$ $\qquad \alpha_{nk} = (u_n^* \alpha u_k) \int e^{-\frac{i}{\hbar}\underline{p_n}\cdot\underline{r} + \frac{i}{\hbar}\underline{p_k}\cdot\underline{r} - i\underline{k}\cdot\underline{r}}$

loss $\alpha_{nk} = 0$, exponent must $= 0$: $-p_n + p_k - \hbar k = 0$;

$\therefore$ $\underline{p_k} = \underline{p_n} + \hbar\underline{k}$ mom. conservation

$\alpha'_{nk} \neq 0$ only if: $\underline{p_n} = \underline{p_k} - \hbar\underline{k'}$;

$\therefore$ $\underline{p_m} + \hbar\underline{k'} = \underline{p_n} + \hbar\underline{k}$.

Then sum $\dfrac{(u_n^* \alpha u_k)(u_k^* \alpha' u_m)}{E_n + h\nu - E_k}$ over possible states with momentum p_k; there will be four, one for each spin, + one for $\pm$ Energy ! $\sum_{\substack{\text{sign of } E \\ \text{spin of } k}}$

spin depend. sometimes interesting : moment, retain its direction.

If not, we must sum of squares of above expression, average over spin of initial quantum. ! $\frac{1}{2}\sum_{\substack{\text{spin } m \\ \text{spin } n}} \left| \sum_{\substack{\text{sign } E \\ \text{spin } k}} \frac{\simeq}{\simeq} \right|^2$. calculate sum by method of Casimir : $\dfrac{(u_m^* \alpha u_k)(u_k^* \alpha' u_m)(E_n + h\nu + E_k)}{(E_n + h\nu)^2 - E_k^2}$

Now $E_k \psi_k = H\psi_k$;

plane wave : $E_k u_k = (c\alpha\cdot p_k - \beta m c^2) u_k$

$\sum_{\substack{\text{spin of } k \\ \text{sign of } E_k}} (u_n^* \alpha (E_n + h\nu + \alpha\cdot p_k - \beta m c^2) u_k)(u_k^* \alpha' u_m)$

$\underline{p_m} + \hbar\underline{k}$.

finally $\frac{1}{2}\sum_{\substack{\text{spin } m \\ \text{spin } n}} |u_n^* P u_m|^2$.

$u_n^* P u_m$

Casimir : look for operator which $= 1$ for + energy, 0 for − energy : it is: $\frac{1}{2}\left(1 + c\alpha\cdot\frac{p}{|E|} - \beta\frac{mc^2}{|E|}\right)u = \begin{cases} u \\ 0 \end{cases}$

$= \frac{1}{2}(1 + \underline{v}\cdot\underline{\alpha} - \beta\mu)u = \begin{cases} u \\ 0 \end{cases}$.

Putting this in matrix element,

will get same as before for positive energy, but 0 for negative —

$u_n^* P(1 + \sigma_m\cdot\alpha - \beta\mu_m)u_m = \begin{cases} u_n^* P u_m & \text{if } E_m > 0 \\ 0 & \text{if } E_m < 0 \end{cases}$.

$\therefore$ $\frac{1}{8}\sum_{\substack{\text{spin+sign of } E \\ m+n}} (u_n^* P(1 + \alpha\cdot\sigma_m - \beta\mu_m)u_m)(u_m^* P^T(1 + \alpha\cdot\sigma_n - \beta\mu_n)u_n$

$= \frac{1}{2} P(1 + \alpha\cdot\sigma_m - \beta\mu_m) P^T(1 + \alpha\cdot\sigma_n - \beta\mu_n)$ averaged over n.

$$I(t) = \int_0^t f(t,s)\,ds$$

$$I(t+\Delta t) = \int_0^{t+\Delta t} f(t+\Delta t, s)\,ds$$

$$\Delta I = I(t+\Delta t) - I(t) = \int_0^{t+\Delta t} f(t+\Delta t, s)\,ds - \int_0^t f(t,s)\,ds$$

$$= \int_0^t \left[f(t+\Delta t, s) - f(t,s)\right] ds + \int_t^{t+\Delta t} f(t+\Delta t, s)\,ds$$

$$\frac{\Delta I}{\Delta t} = \int_0^t \frac{f(t+\Delta t, s) - f(t,s)}{\Delta t}\,ds + \frac{1}{\Delta t}\int_t^{t+\Delta t} f(t+\Delta t, s)\,ds$$

$$\therefore \frac{dI}{dt} = \int_0^t \frac{\partial f}{\partial t}\,ds + f(t,s)$$

If $\alpha = \alpha'$ (polarization the same for inc. + scatt.) then we have:

$$P = E_n + h\nu + \beta m c^2 - c\,\underline{\alpha}\cdot(\underline{p}_n + h\underline{k}_n) + 2\alpha_n(p_{nx} + \overset{\to 0}{h k_{nx}})$$

$\therefore P$ is of form $A + B\alpha + C\beta$. then $(1 + \underline{\alpha}\cdot\underline{\sigma}_n - \beta\mu_n)(1 + \underline{\alpha}\cdot\underline{\sigma}_n - \beta\mu_n)$

$= (1 + \underline{\sigma}_n\cdot\underline{\sigma}_n + \mu_n\mu_n)$.

then:

$$P(1 + \underline{\alpha}\cdot\underline{\sigma}_n - \beta\mu_n)\,P^{\dagger}(1 + \underline{\alpha}\cdot\underline{\sigma}_n - \beta\mu_n)$$

$$= A^2(1 + \underline{\sigma}_n\cdot\underline{\sigma}_n + \mu_n\mu_n) - 2AC(\mu_n + \mu_n) + \ldots \text{etc} -$$

Read in Heitler – better than Klein – Nishina original paper –

Compton scattering probability becomes greater than photoel. effect for very high energies – $< 10^5$ eV photoel; $10^5 - 10^8$ Compton effect, $> 10^8$, pair production

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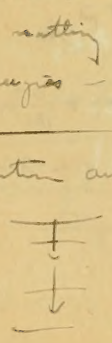
Two-quantum annihilation – positron disappears in 10^{-10} sec.



$x^\alpha p^\beta - p^\beta x^\alpha$

$\cancel{px - xp = -i\hbar}$

$\cancel{-xp - px = i\hbar}$

$\cancel{x^2p - px^2 =}$ $xxp - xpx + xpx - pxx = x[xp] + [xp]x$

$[xp]$ $\quad [x^2p] = x[xp] + [xp]x$

$= x\,i\hbar + i\hbar\,x = 2i\hbar\,x$

$[xp^2] = [xp]p + p[xp]$

$= i\hbar\,p + p\,i\hbar = 2i\hbar\,p$

$xpp - ppx$

$pp - pxp + pxp - ppx$

$[xp]p + p[xp]$

$[AB, C] = ABC - CAB = ABC - ACB + ACB - CAB$

$= A[B,C] + [A,C]B$

$[AB, C] = A[B,C] + [A,C]B$

$\Delta\psi + \frac{m}{\hbar^2}(E-H)\psi = 0$

$[a^2, b] = a[a,b] + [a,b]a$

$[xH - Hx]$

$p \qquad \dot{y}H_{ij} - H\dot{y}_{ij} = (AH - HA)_{ij} = A_{il}H_{lj} - H_{il}A_{lj}$

$= A_{ij}E_j - A_{ij}E_i$

$= A_{ij}(E_j - E_i)$

$= i\hbar\,\dot{A}_{ij}$

$A_{ij} = a_{ij}e^{\frac{i(E_i - E_j)t}{\hbar}}$

$\dot{A}_{ij} = \frac{i}{\hbar}(E_i - E_j)$

$\therefore [AH] = -i\hbar\,\dot{A}$

$$\sum_{mn} A_{mn} \sum_{k} S^{-1}_{km} S_{nk}$$

$$\sum_{k} S_{nk} S^{-1}_{km} = (S S^{-1})_{nm} = \delta_{nm}$$